

Program & Abstracts

of the

First International Workshop on

AMORPHOUS AND NANOSTRUCTURED CHALCOGENIDES

- Fundamentals and Applications -

Bucharest, Romania, June 25-28, 2001

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Scope

The workshop is intended to be a forum for discussions and exchange of ideas and results on properties and phenomena related to non-crystalline chalcogenides. It is aimed at physicists, chemists and material scientists interested in this field.

Topics:

- State of the art in physics and chemistry of non-crystalline chalcogenides
- New developments in nanostructured chalcogenides: multilayers, wires, dots
- Nanocrystalline chalcogenides versus amorphous chalcogenides
- Applications. Modern devices for optoelectronics
- Chalcogenides and glass science
- Other glasses as partners of the chalcogenides glasses

Honorary Director: Radu Grigorovici,
Romanian Academy

Director: Mihai A. Popescu, NIMP, Bucharest

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Monday, June 25, 2001

- 8.00 - 9.00 Registration
9.00 - 9.30 Opening Ceremony (Aula Magna, Romanian Academy - Calea Victoriei, No. 125)
9.30 - 10.00 Celebration: Prof. Radu Grigorovici at his 90th anniversary

Plenary Session

Chairmen: A. Kolobov, M. Ribes

- 10.00 - 10.45 G. Lucovsky, North Carolina State University, USA
Electronic structure, amorphous morphology and thermal stability of transition metal oxide and chalcogenide alloys
10.50 - 11.25 K. Shimakawa, V. A. Ganjoo, Gifu University, Japan
Current understanding of photoinduced volume and bandgap changes in amorphous chalcogenides

11.30 - 12.00 **Coffee break**

Plenary session

Chairmen: S. Hosokawa, V. Minaev

- 12.00 - 12.30 K. Tanaka, Hokkaido University, Japan
The charged defect exists?
12.35 - 13.05 P. Boolchand, University of Cincinnati, USA
The intermediate phase in chalcogenide glasses
13.10 - 13.40 M. Popescu, National Institute of Materials Physics, Bucharest, Romania
Modelling of the atomic scale structure of non-crystalline chalcogenides

13.45 - 15.00 **Lunch (canteen of Bucharest University)**

Plenary session

Chairmen: Y. Messaddeq, A. Kikineshi

(Aula Magna, University of Bucharest - Bulevardul M. Kogalniceanu, No. 60)

- 15.00 - 15.30 A. Kolobov, Tsukuba Research Center, Japan
Nanometer-scale mechanism of reversible photostructural changes in chalcogenide glasses
15.35 - 16.05 H. Jain, Lehigh University, USA
Light-induced changes in the structure of chalcogenide glasses
16.10 - 16.35 M. Frumar, Z. Černošek, T. Wágner, B. Frumarová, University of Pardubice, Czech Republic
Photoinduced changes of structure and properties of binary and ternary amorphous chalcogenides
16.40 - 17.05 V. Lyubin, M. Klebanov, Ben-Gurion University, Beer-Sheva, Israel
Interaction of polarized light with chalcogenide glasses

17.05 - 17.30 **Coffee break**

Plenary session

Chairmen: C. Raptis, P. Baltă

- 17.30 - 18.00 G. N. Greaves, G. Sankar, L. Colyer, C. Alétru, University of Wales, UK
Characterising the nanoparticle structure and stability of cadmium chalcogenides incarcerated in zeolitic frameworks
18.05 - 18.35 D. Nesheva, Institute of Solid State Physics, Sofia, Bulgaria
Nanoparticle layers of CdSe in various multilayer structures
18.40 - 19.05 W. Hoyer, I. Kaban, Th. Halm Institute of Physics, TU Chemnitz, Germany
Influence of the integration limits on the shape of pair correlation functions of non-crystalline materials
20.00 - 22.00 Welcome Party (in the House of the Scientists, Piața Alexandru Lahovari, No. 3)

Tuesday, June 26, 2001

Plenary session

Chairmen: E. Shimakawa, S. Asokan

- 8.30 - 9.00 A. M. Andriesh, President of the Academy of Sciences, Moldova
Non-linear absorption in non-crystalline semiconductors due to interaction of light with non-equilibrium excited carriers and phonons
- 9.05 - 9.45 I. Balberg, The Hebrew University, Jerusalem, Israel
Transport and phototransport in amorphous and nanostructured semiconductors
- 9.50 - 10.20 V. Arkhipov, E. V. Emelianova, H. Bässler, Philipps University, Marburg, Germany
Equilibrium carrier transport in disordered organic semiconductors
- 10.25 - 10.55 A. Aldea, M. Nita, National Institute of Materials Physics, Bucharest, Romania
Negative magnetoresistance and electron-electron interaction in disordered 2D mesoscopic systems

11.00 - 11.30 Coffee break

Plenary session

Chairmen: Ke. Tanaka, J. M. Saiter

- 11.30 - 12.00 A. Ganjoo, K. Shimakawa, Gifu University, Japan
Transient and metastable photodarkening in amorphous chalcogenides
- 12.05 - 12.35 C. Main, D. Nesheva, University of Abertay Dundee, UK
Transient photocurrent techniques as a means of characterising amorphous semiconductors
- 12.40 - 13.10 Y. Wang, T. Nakaoka, K. Murase, Osaka University, Japan
Dynamics of Ge-Se glasses at stiffness transition
- 13.15 - 13.45 M. Ribes, E. Bychkov, A. Pradel, University Montpellier 2, France
Ion transport in chalcogenide glasses: dynamics and structural studies

13.50 - 15.00 Lunch

Plenary session

Chairmen: K. Petkov, V. Lyubin

- 15.00 - 15.30 C. Raptis, National Technical University of Athens, Greece
Structural Raman studies of Ge-based chalcogenide glasses
- 15.35 - 16.00 Y. Messaddeq, S. H. Messaddeq, M. Siu Li, D. Ležal, S. J. L. Ribeiro, Chemistry Institute, Araraquara, Brasil
Investigation of photoinduced effect in GaGeS based glasses and thin films
- 16.05 - 16.25 A. Kikineshi, Uzhgorod University, Ukraine
Light - stimulated structural transformations and optical recording in amorphous nanolayered structures
- 16.20 - 18.00 *Poster Session I (P1 - P41)*
- 18.00 - 20.00 Bucharest Tour
Visit to Parliament Building

Wednesday, June 27, 2001

Plenary Session *Chairmen: M. Frumar, C. Main*

- 8.30 - 9.00 J. S. Sanghera, I. D. Aggarwal et al.,
Naval Research Laboratory, Washington DC, USA
Applications of chalcogenide glass optical fibers at NRL
- 9.05 - 9.35 K. Richardson et al., University of Central Florida, USA
Engineering chalcogenide glass materials for integrated optics applications
- 9.40 - 10.10 T. Ohta, Matsushita Electric Industrial Co., Osaka, Japan
Phase-change optical memory promotes the DVD optical disks
- 10.15 - 10.45 M. Stuchlik, P. Krecmer, S. R. Elliott, University of Cambridge, UK
Optical actuation in amorphous chalcogenides

10.50 - 11.15 **Coffee break**

Plenary Session *Chairmen: J. Sanghera, H. Jain*

- 11.15 - 11.45 M. Schieber, Hebrew University of Jerusalem, Israel
Starting materials purifications and characterization
- 11.50 - 12.20 M. Churbanov et al., Institute of Chemistry of High Purity Substances, Nizhny
Novgorod, Russia
High-purity glasses based on arsenic chalcogenides
- 12.25 - 12.55 J. Heo, Pohang University, Republic of Korea
Control of phonon vibration in chalcogenide glasses for high-performance
1.3 μm - window fiber-optic amplifiers
- 13.00 - 13.30 A. Pradel et al., Université Montpellier II, France
Chalcogenide glasses as sensitive membranes for the of ions detection in solution

13.35 - 15.00 **Lunch**

Plenary Session *Chairmen: I. D. Aggarwal, P. Boolchand*

- 15.00 - 15.30 I. V. Scripachev et al., Institute of Chemistry of High Purity Substances, Nizhny
Novgorod, Russia
Optical and mechanical characteristics of fibers made of arsenic chalcogenides
- 15.35 - 16.05 D. Ležal, J. Zavadil, Laboratory of Inorganic Materials, Prague, Czech Republic
Chalcogenide glasses for optoelectronics
- 16.10 - 16.40 K. D. Tsendin, A. F. Joffe, Physico-Technical Institute, St. Petersburg, Russia
Physical properties of doped chalcogenide glassy semiconductors which are governed
by the interaction of negative-U defects and impurity states
- 16.45 - 17.05 V. Vlasov, Uzhgorod National University, Ukraine
Effective holographic record on thin films of chalcogenide semiconductors
- 17.10 - 17.30 O. Shpotyuk et al., Institute of Materials, Lviv, Ukraine
Radiation defects in As-Ge-S studied by position annihilation techniques

17.35 - 19.30 *Poster Session II (P42 - P82)*

Dinner party: 20.30 - 22.30

Thursday, June 28, 2001

Plenary Session

Chairmen: G. N. Greaves, W. Hoyer

- 8.30 - 8.55 S. Hosokawa, Philipps University of Marburg, Germany
Atomic and electronic structures of glassy $\text{Ge}_x\text{Se}_{1-x}$ around the stiffness threshold composition
- 9.00 - 9.20 V. S. Minaev, Research Institute of Materials Science and Technology, Moscow, Russia
Polymorphic-crystalloid structure and relaxation processes in some chalcogenide glass-forming substances
- 9.25 - 9.45 S. Asokan, Indian Institute of Science, Bangalore, India
Electrical switching in chalcogenide glasses - some newer insights
- 9.50 - 10.10 J. M. Saiter, Université de Rouen, France
Physical ageing in chalcogenide glasses
- 10.15 - 10.35 M. S. Iovu et al., Center of Optoelectronics, Chisinau, Moldova
Spectroscopic studies of rare - earth doped As_2S_3 glasses
- 10.40 - 11.00 P. Baltă, University "Polytechnica", Bucharest, Romania
Ideas concerning the obtainment of non-crystalline materials by melt undercooling
- 11.05 - 11.20 Commemoration: Prof. Razoum Andreichin (1911-1997)
- 11.20 - 11.35 E. Skordeva, Institute of Solid State Physics, Sofia, Bulgaria
Photoelectret properties and high - field polarization in chalcogenide glasses and thin films
- 11.40 - 12.00 **Coffee break**
- 12.00 - 13.00 Round Table: New concepts, tools and trends for applications
Key speakers: K. Shimakawa (science)
I. D. Aggarwal (technology)
- 13.00 - 13.15 Awarding Ceremony: Boris T. Kolomiets Award for the best paper in the Workshop
Stanford R. Ovshinsky Award for Excellence in
Non-crystalline Chalcogenides
- 13.15 - 13.30 **Short break**
- 13.30 - 14.00 Closing Ceremony

Friday, June 29, 2001

- 8.00 - 20.00 Trip to "Dracula Castle" - Bran

Abstracts of Plenary Papers

ELECTRONIC STRUCTURE, AMORPHOUS MORPHOLOGY AND THERMAL STABILITY OF TRANSITION METAL OXIDE AND CHALCOGENIDE ALLOYS

Gerald Lucovsky

Departments of Physics, Electrical and Computer Engineering, and Materials Science
and Engineering, North Carolina State Univ., Raleigh, NC 27695, USA

This paper is dedicated to the 90th birthday celebration of Professor Radu Grigorovici whose contributions to our collective understanding of the chemical bonding and atomic structure of amorphous chalcogenides have made a significant impact on the research that has addressed optical and electrical properties, as well as technological applications. This paper extends the fundamental bonding approach of Professor Grigorovici to non-crystalline transition metal oxides and their silicate and aluminate alloys. This approach complements other classification schemes for oxide glasses and thin films that have been based on the average number of bonds, or bonding constraints per atom. When combined with a molecular orbital, MO, description of the electronic structure at the transition metal atom sites, the insights derived from in this way are directly applicable to the electronic properties of alternative high-k gate dielectrics: ZrO_2 and HfO_2 , and their binary silicate alloys, $(\text{SiO}_2)_{1-x}(\text{Zr}(\text{Hf})\text{O}_2)_x$. These materials have been proposed as replacements for thermally grown SiO_2 in advanced Si CMOS devices.

A novel and systematic approach based on bond ionicity provides a basis for understanding systematic trends in the amorphous morphology of non-crystalline elemental and binary oxide alloys. This classification is based on an empirically defined bond ionicity scaling parameter: the difference between the Pauling electronegativities of oxygen, and the metal or semiconductor atom of the oxide, $\Delta X = X(\text{O}) - X(\text{M}, \text{S})$. Bond-ionicity *distinguishes* three groups of non-crystalline elemental oxides with different amorphous morphologies: i) $\Delta X < 1.6$ – continuous random networks, crn's, such as SiO_2 , B_2O_3 , and P_2O_5 , ii) $1.6 < \Delta X < 2.0$ – modified crn's networks with 'interstitial' ions such as Al_2O_3 and Ta_2O_5 , and iii) $\Delta X > 2$ – structure based on the random close packing of ions as in $\text{Zr}(\text{Hf})\text{O}_2$, and $\text{Y}(\text{La})_2\text{O}_3$. The approach has been extended to binary oxide alloys using compositionally averaged X's, and to transition metal chalcogenides as well.

Systematic trends between atomic and network bonding, and thermal stability have been identified for thin film elemental oxides, Al_2O_3 , Ta_2O_5 and ZrO_2 , and binary silicate alloys such as $(\text{SiO}_2)_{1-x}(\text{Zr}(\text{Hf})\text{O}_2)_x$. As ΔX increases, the coordination of the metal atom increases, and thermal stability with respect to crystallization decreases. ZrO_2 , Ta_2O_5 and Al_2O_3 crystallize respectively at temperatures $< 500^\circ\text{C}$, 700°C and 900°C . The coordination of Zr increases from 4 in low concentration alloys, $x \sim 0.2$, to 8 for $x \geq 0.5$. Application of MO theory shows that these changes in atomic coordination of Zr require changes in the symmetries of the Zr d-states that contribute to a dynamic infrared effective charge, thereby providing a microscopic mechanism for marked enhancements in the dielectric constant at low Zr concentrations ~ 6 atomic %.

The bond-ionicity approach has also been applied to amorphous morphology and properties of transition metal chalcogenide alloys, e.g., Ni in As_2Se_3 based chalcogenide alloys. Since the X's of S and Se are reduced with respect to $X(\text{O})$, scaling based on bond ionicity is compressed. The energies of the transition metal electronic states relative to the conduction and valence bands of a chalcogenide alloy host as estimated from MO theory, and the occupancy of these states and the transition metal concentration are the important factors in promoting a transition from insulating to metallic conductivity as a function of increasing metal atom content.

Research supported by the ONR, AFOSR and SRC/Sematech Front End Processes Center.

CURRENT UNDERSTANDING OF PHOTOINDUCED VOLUME AND BANDGAP CHANGES IN AMORPHOUS CHALCOGENIDES

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For a long time, the terms "photodarkening (PD)" and "photostructural changes (PSC)" had been equivalently used in the study of photoinduced changes in amorphous chalcogenides, i.e. PD is just the result of PSC. However, a recent discovery, e.g. the rate of PD is slower than that of the photo-induced volume changes (PVC), may suggest that PVC and PD are due to independent mechanisms [1]. The study of the changes in the bandgap and volume of amorphous chalcogenides induced by photoillumination has renewed attention.

In the present talk, the recently obtained interesting results on the reversible PD and PVC for As-based chalcogenides ($a\text{-As}_2\text{S}(\text{Se})_3$ films) will be reviewed. Through the study of time evolution of these changes during illumination, we have found that there exists the *transient* (only observed under illumination) and the *metastable* (after illumination) changes in PD and PVC [2,3]. The dynamics of PD are also discussed in terms of the model of photon-assisted site switching, in which the effective medium approximation is used in the calculation of the change of optical absorption [4].

All the data seem to be explained by the repulsive layer model [5], in which macroscopic expansion and slip motions of layered clusters is taken into account for PVC and PD to occur.

References

- [1] Ke.Tanaka, Phys. Rev. B 57, 5163 (1998).
- [2] Ashtosh Ganjoo, Y. Ikeda, and K. Shimakawa, Appl. Phys. Lett. 74, 2119 (1999).
- [3] Ashtosh Ganjoo et al., in preparation.
- [4] Ashtosh Ganjoo, K. Shimakawa, H. Kamiya, E. A. Davis, J. Singh, Phys. Rev. B 62, R14601 (2000).
- [5] K. Shimakawa, N. Yoshida, Ashtosh Ganjoo, Y. Kuzukawa, J. Singh, Philos. Mag. Lett. 77, 153 (1998).

THE CHARGED DEFECT EXISTS?

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Researches upon amorphous semiconductors started in the middle of 20 century, and now at the beginning of 21 century, we have obtained a fair amount of experimental data, several working hypotheses, and a few basic ideas. Among the hypotheses, specifically related to the chalcogenide glass is the charged-defect (and valence-alternation pair) model proposed by Mott et al. and Koster et al. The model has been repeatedly employed for interpreting many characteristics such as AC conductivity. However, since the defect (D^+ and D^-) is inherently ESR-inactive and the density is estimated to be smaller than ppm levels, direct evidence of the existence has not been presented. On the other hand, other possibilities for gap states have also been suggested by several researchers.*

I have studied the electronic density of gap states, which govern optical absorption spectra, in bulk As_2S_3 glass. Several observations suggest that the Urbach edge reflects tail states (~ 10 at.%) above the valence band, which possibly arise from fluctuation of interlayer interaction. On the other hand, it is suggested that the weak absorption tail arises from antibonding states of As-As wrong bonds (~ 0.5 at.%), which are located below the conduction band. These gap states are much denser than the charged defects predicted. Accordingly, it is difficult to envisage that the charged defects govern electronic properties of As_2S_3 glass.

References

- [1] V. Halpern, *Philos. Mag.*, **34**, 331 (1976).
- [2] S. R. Ovshinsky, D. Adler, *Contemp. Phys.* **19**, 109 (1978).
- [3] D. Vanderbilt, J. D. Joannopoulos, *Phys. Rev. B* **23**, 2596 (1981).
- [4] Y. Watanabe et al., *J. Non-Cryst. Solids* **95&96**, 365 (1987).

THE INTERMEDIATE PHASE IN CHALCOGENIDE GLASSES

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A network of polymeric chains (intrinsically floppy) will spontaneously become rigid upon progressive cross-linking, when the connectivity acquires a threshold value. For a 3d network constrained by central- and angular-forces, a single *floppy to rigid transition* is predicted at a mean coordination number, $\langle r \rangle = 2.40$, and it corresponds to an average count of 3 constraints per atom.

Recent thermal and optical experiments on Chalcogenide glasses have shown¹ that there are in fact *two* and not *one* transition as first predicted by mean-field constraint counting algorithms. The two transitions define the limits of an *intermediate phase* that separates the *floppy*- from the *stressed rigid*- phase. Glassy networks in the intermediate phase are rather special. They are not only stress-free as revealed by the absence of a *non-reversing heat flow term near T_g* in Temperature Modulated Differential Scanning Calorimetry measurements. But they also display a *sub-linear elastic power-law* in contrast to a *super-linear* behavior observed in the stressed rigid phase from Raman scattering measurements.

The compositional width of the *intermediate phase* appears to be intimately tied to the details of glass structure. In glass systems where the evolution of structure with connectivity is *stochastic* in nature ($\text{Ge}_{0.25}\text{S}_{0.75-y}\text{I}_y$), the width of the intermediate phase is found to vanish. On the other hand, in glass systems where a multitude of optimally constrained network building blocks can co-exist ($\text{Ge}_x\text{As}_x\text{Se}_{1-2x}$), self-organization can occur², and contribute to the width of the *intermediate phase*. These cases documented in laboratory experiments, apparently represent the *two extreme descriptions of rigidity onset modelled numerically*³. In the chalcogenide glass system mean-field theory is upheld because of the random network structure, while in the chalcogenide glass system mean-field theory completely breaks down because of substantial self-organization of the network. Some broad consequences of the discovery of the *intermediate phase* in network glasses will be discussed.

References

- [1] P. Boolchand, D. Selvanathan, Y. Wang, D. G. Georgiev, W. J. Bresser, in Properties and Applications of Amorphous Materials, edited by M. F. Thorpe, L. Tichy, (Kluwer Academic Publishers, Dordrecht, 2001), Vol. 9, p. 97-132.
- [2] Y. Wang, P. Boolchand, M. Micoulaut, Europhys. Lett., **52**, 633 (2000).
- [3] M. F. Thorpe, M. V. Chubynsky, D. J. Jacobs, J. C. Phillips **266-269**, 859 (2000).

MODELLING OF THE ATOMIC SCALE STRUCTURE OF NON-CRYSTALLINE CHALCOGENIDES

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The atomic scale structure of non-crystalline chalcogenides is still a challenging problem. With the advent of new discoveries in the field of disordered chalcogenides, as e.g. the stable photo-induced anisotropy, the questions related to the atomic scale structure and modifications under various external factors become more and more important.

Starting from ball and sticks models, and, then, using computer arrays of coordinates, it was possible to find realistic structures for different members of the chalcogenide systems: As-Se, Ge-Se, Ge-Se, As-Se-Ge, As-Te-Ge, etc...

The rough arrays of coordinates were relaxed by using a computer Monte Carlo procedure for the minimization of the free energy calculated in small clusters of atoms. The interaction between atoms were introduced on the basis of well-known covalent and weak van der Waals bonds characterized by specific force constants.

The photo-darkening and photo-bleaching, as well as the photo-induced anisotropy in amorphous chalcogenides, received an elegant explanation in the frame of models with specific bond switching occurring in disordered layer-like configurations.

NANOMETER-SCALE MECHANISM OF REVERSIBLE PHOTOSTRUCTURAL CHANGES IN CHALCOGENIDE GLASSES

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In this talk the historical overview of reversible photostructural changes is first given. Description of the photostructural changes within the framework of the configuration-coordinate model and early microscopic models is followed by the results of the authors' recent in-situ experiments. Based on in-situ EXAFS, Raman scattering, and ESR studies the nanometer-scale of the reversible photostructural changes is established. The structural change is demonstrated to consist in the formation of dynamic interchain (interlayer) chalcogen-chalcogen bonds and subsequent bond switching. Recent ab-initio calculations confirm the suggested mechanism.

Other photo-induced phenomena such as photo-induced anisotropy and photocrystallisation are discussed in relationship with the proposed nanometer-scale mechanism.

LIGHT-INDUCED CHANGES IN THE STRUCTURE OF CHALCOGENIDE GLASSES

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Many properties of semiconducting glasses based on chalcogens are known to be sensitive to the light of energy $h\nu \approx E_g$, where ν is the frequency of light and E_g is the bandgap (typically 1-3 eV). The photons may affect the volume, amorphization, devitrification, mechanical (e.g. plasticity), rheological (e.g. viscosity), optical (e.g. darkening, birefringence, luminescence), electrical (e.g. conductivity, dielectric constant), or the chemical (e.g. oxidation, etching, dissolution, doping) properties of glass. In general, the photo-induced changes may be classified into three categories depending on their stability: (a) permanent changes which cannot be recovered unless the sample is prepared again, (b) metastable changes which can be reversed by heating the sample to the glass transition temperature, and (c) temporary changes which can be reversed simply by removing the light source, or exposing the specimen to appropriate light subsequently. The fundamental origin of these fascinating light-induced phenomena may be traced in the changes that occur in the electronic and atomic structure of the glass, which will be the focus of this presentation.

The various photo-induced effects arise from the changes that occur in glass after its electrons are excited by light of the appropriate frequency. In turn, the electronic excited state causes reorganization of atomic structure. Therefore, we have been monitoring the effect of light on the electronic as well as the physical structure of arsenic selenide glasses as a model system. Both the temporary and permanent light-induced changes are recorded using high-resolution x-ray photoelectron spectroscopy (XPS) and extended x-ray absorption fine structure (EXAFS) analysis under in situ laser irradiation. In general, the results show that the lone pair states of the chalcogen atoms are most easily affected by the light. Also the physical environment around the chalcogen atoms shows maximum alteration, which is partly recovered by removing the light. Careful experiments indicate sensitivity of the observed changes to the presence of oxygen/air during irradiation. The kinetics of photo-induced reaction with air is determined by angle resolved XPS and atomic force microscopy of the surface.

References

- [1] K. Shimakawa, A. Kolobov, S.R. Elliott, Photoinduced effects and metastability in amorphous semiconductors and insulators, *Adv. Phys.* 44, 475 (1995).
- [2] K. Tanaka, Photoinduced structural changes in chalcogenide glasses, *Rev. Solid. St. Sci.* 4, 641 (1990).

PHOTOINDUCED CHANGES OF STRUCTURE AND PROPERTIES OF BINARY AND TERNARY AMORPHOUS CHALCOGENIDES

M. Frumar, Z. Černošek, T. Wágner and B. Frumarová^a

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The exposure of chalcogenide glasses and thin films by the light with energy close to optical gap or higher can change the structure and physicochemical properties of the amorphous material. In compounds, many of these changes can be ascribed to changes of chemical bonds statistics, very often to photochemical synthetic or photolytic reactions. The changes of bond statistics were checked by several structure-sensitive methods; in this paper, the results of IR and Raman spectra study were emphasized. While the photochemical changes can explain many features of photostructural effects, the other factors play also a role and should be considered.

New results in this area are reviewed and models for description of photoinduced changes are discussed.

The study was partly supported by grant No. 203/00/085 of Czech Grant Agency and by project LN00A028 of Czech Ministry of Education; both are gratefully acknowledged.

INTERACTION OF POLARIZED LIGHT WITH CHALCOGENIDE GLASSES

V. Lyubin, M. Klebanov

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In the first part of the paper we summarize the results of our study of photoinduced optical anisotropy in thin film and bulk samples of different chalcogenide glasses. We distinguish three ranges of exciting photons energy.

1. Above-band-gap excitation, which is studied by means of measurement of light transmission in thin film samples. Creation of photoinduced defects and their next orientation and reorientation are the reasons of dichroism and birefringence observed in this range.

2. Sub-band-gap excitation is investigated by studying of light transmission and scattering in bulk glasses. Creation of anisotropically scattering defects is assumed to be the reason of anisotropy in this case.

3. Super-band-gap excitation is studied in both thin film and bulk glassy samples due to application of differential reflectance spectroscopy. We succeeded to show that in this case not only defects but also main covalent bonds of the glass can be oriented and reoriented in that spectral interval.

We consider also some interesting results obtained recently in different research groups. Among them: polarization-dependent photocrystallization of some amorphous films, polarization-dependent photodoping of chalcogenide films by metals, polarization-dependent optomechanical effect and photoinduced anisotropy in the ion-conducting amorphous chalcogenide films.

At last, new results which we and our colleagues obtained at studying photoinduced anisotropy in the photobleaching chalcogenide films and new phenomenon - photoinduced anisotropy of photoconductivity in chalcogenide films will be considered.

CHARACTERISING THE NANOPARTICLE STRUCTURE AND STABILITY OF CADMIUM CHALCOGENIDES INCARCERATED IN ZEOLITIC FRAMEWORKS.

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The internal microporous structure of zeolites can serve as substrates on which to nucleate and confine nanosized semiconducting precipitates [1]. Other groups have detected these optically by diffuse reflectance and imaged by conventional TEM. We show how the novel combination of *in situ* X-ray Absorption Spectroscopy (XAFS), Small Angle X-ray Scattering (SAXS) and X-ray Diffraction (XRD) can be used to fully characterise nanoparticle growth and the eventual collapse of the zeolite host [2]. The composition and local atomic structure are recorded by XAFS, the particle size and surface roughness by SAXS and the crystalline integrity of the encapsulating microporous substrate by XRD. Examples are taken of the incarceration of CdS in zeolite:A and its eventual decomposition at elevated temperatures. Prepared from H₂S treatment of calcined Cd exchanged Na zeolite:A, this synthesis is compared with alternative solution methods which have recently been perfected. Combined X-ray techniques have also been used to identify CdO nanoparticles in zeolite:A and zeolite: Y, and their growth charted with increasing temperature. We find, for instance, that the size of chalcogenide nanoparticles is indeed restricted by zeolite pore dimensions and that subsequent temperature-induced growth destabilises the zeolitic structure, resulting in the nucleation of spinel and stuffed quartz structures in an amorphous matrix [3]. Finally we review the equivalent effect of pressure at ambient temperature in promoting zeolite collapse, interpreting zeolitic stability in the context of Rigidity Percolation Theory [2].

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NANOPARTICLE LAYERS OF CdSe IN VARIOUS MULTILAYER STRUCTURES

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Continuous and discontinuous nanoparticle layers of CdSe have been produced by sequential physical vapor deposition of CdSe and some 'matrix' materials. The nominal thickness of CdSe layers has been varied between 1 and 10 nm. Amorphous SiO_x or GeS_2 as well as polycrystalline ZnSe thin films have been used as "matrix" materials. Continuous nanocrystalline CdSe layers have been fabricated when the 'matrix' layer thickness varied between 2.5 and 10 nm, while discontinuous CdSe nanoparticle layers were obtained when the 'matrix' layer thickness was in the region of 20-120 nm.

High angle X-Ray diffraction and High-resolution electron microscopy have been used to prove the formation of CdSe nanoparticles. A significant difference has been found in the nanoparticle size determined by both methods, which has been ascribed to appreciable lattice deformations. Electron micrographs have shown that the discontinuous layer consisted of particles with nearly spherical form, whose spatial distribution followed the surface morphology of the 'matrix' films. It has been shown that annealing of SiO_x -CdSe films at temperatures higher than 900 K leads to the formation of isolated CdSe nanoparticles homogeneously distributed in the matrix.

Dark current measurements were carried out on films comprising continuous (multilayers) and discontinuous (composite films) CdSe layers. Size induced changes of the room temperature conductivity and dark current activation energy have been observed in SiO_x -CdSe films. It has been concluded that in both multilayers and composite films charge transport, in the layer plane, involves networks of CdSe nanocrystals contacting with each other. It has been found that in the SiO_x /CdSe multilayers charge transport is controlled by potential barriers for electrons existing at the CdSe-CdSe interface while in the SiO_x -CdSe composite films those potential barriers do not affect appreciably the charge transport, due to the great conductivity increase, induced by the SiO_x matrix.

INFLUENCE OF THE INTEGRATION LIMITS ON THE SHAPE OF PAIR CORRELATION FUNCTIONS OF NON-CRYSTALLINE MATERIALS

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Experimentally determined distances of nearest neighbours and the coordination number of the first coordination sphere as well as corresponding values for higher coordination spheres are important parameters for the description of the structure of non-crystalline matter. As is well known, the scattering pattern can only be measured over some finite range in reciprocal space, and consequently the resulting pair distribution functions $g(r)$ differ from the ideal pair distribution functions (termination or truncation errors).

In principle the scattering intensity can be measured down to $Q = 0$, $Q = (4\pi/\lambda)\sin\theta$, where Q is the magnitude of the scattering vector, λ is the used wavelength and θ is half the scattering angle. But experimental limitations and in some cases additional small angle scattering lead to a lower limit Q_{\min} for each scattering experiment. On the other hand for a certain wavelength each diffraction experiment is limited by a maximum wave vector transfer of $Q = 4\pi/\lambda$.

On the example of Te-based glasses and using an extrapolation function $S(Q) = S(0) + AQ^2$ in the region $Q < Q_{\min}$ it will be shown that termination at $Q_{\min} > 0$ rather strongly influences the real space region around the first peak of $g(r)$ especially its left flank. $S(0)$ is determined by the thermodynamic limit and the fitting parameter A results from fitting the extrapolation function to the experimental $S(Q)$ at $Q = Q_{\min}$.

With increasing Q_{\max} the height of the first peak increases while the peak width and the coordination number decrease. One possible way to estimate truncation effect errors is to make an educated guess on $S(Q)$ for $Q > Q_{\max}$. For the extrapolation we used the function

$$S(Q) = 1 + c_1 \cos(c_2 Q - c_3) \exp\{-c_4 Q\} / Q$$

which enables us to obtain an analytical expression for the pair correlation function $g(r)$ also for infinite Q_{\max} . The parameters $c_1 \dots c_4$ have been determined by a least squares fit of the high Q -region of experimental $S(Q)$. Besides studying the influence on first peak width and coordination number the extrapolation may help to make visible ghost peaks.

NON-LINEAR ABSORPTION IN NON-CRYSTALLINE SEMICONDUCTORS DUE TO INTERACTION OF LIGHT WITH NON-EQUILIBRIUM EXCITED CARRIERS AND PHONONS

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There have been found by many authors that transport phenomena in non-crystalline semiconductors including chalcogenide glasses are conditioned by interaction of excited non-equilibrium carriers with traps distributed quascontinuously in the forbidden gap and with non-equilibrium phonons. However the excitation of non-equilibrium carriers and phonons in such systems also leads to many peculiarities of optical properties. In this report a review will be given concerning photoinduced non-stationary absorption and non-linear absorption.

The phenomena conditioned by cooperative generation of non-equilibrium localized phonons will be described too. The mentioned mechanisms were applied for interpretation of photoinduced absorption in chalcogenide fibers, for non-linear light absorption in chalcogenide thin films under pulse excitation, including short laser pulses.

The observed hysteresis dependence of the output light intensity as a function of the input light intensity was explained using the mentioned above mechanisms. The data of photoinduced absorption have been used for determining of drift mobility in As_2S_3 fibers.

TRANSPORT AND PHOTOTRANSPORT IN AMORPHOUS AND NANOSTRUCTURED SEMICONDUCTORS

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The physical opposite extreme of the crystalline material is the amorphous system in which the Bloch concept of “crystal momentum” does not hold. Correspondingly, the potential fluctuations in systems [1] such as amorphous chalcogenides yield localized bandtail states. If the energy of the carrier is high enough it can wander between “extended states” in a classical-like percolative path of an infinite extent. If its energy is lower, the carrier is a priori localized and only quantum mechanical tunneling and/or hopping enable it to wander throughout the system. [2] While the above mechanisms determine the mobility of the charge carriers, their concentration under optical excitation is determined by the kinetics and charge neutrality that govern the recombination in the bandtails. It turns out that this behavior is very different than the one observed for discrete levels in crystalline [3] semiconductors or tetrahedrally bonded amorphous [4] semiconductors.

When the system consists of small (less than 100 Å in diameter) semiconducting particles that are embedded in an insulating matrix we refer to the nanostructured system as a nanoparticle (or a quantum dot) semiconductor composite. The important characteristic of such composites is that their optical and electrical properties depend on the diameter of the particles. The conduction between two such particles is by tunneling, but it is hindered by the “Coulomb blockade” that results from the charging of adjacent particles due to the transfer of a carrier from one particle to the other under the presence of an applied bias. [5] This causes, as in granular metals, the selection of an optimal conduction path and consequently, bias induced opening of selected conduction paths. [6] The phototransport in the composites is a result of the optical excitation within the nanoparticles and the transport is in the same route as in the dark. However, the lifetime of the carriers is determined by recombination at surface-like states, or by the break-up of the induced particle-confined excitons. As the density of the nanoparticles becomes high enough both, the transport and the phototransport properties, change to those expected for a macroscopic percolative network of a polycrystalline-like semiconductor. This is since in semiconductor particles, unlike in metal particles, the semiconductor-insulator boundary may play a dominant role in the transport and recombination processes [7]. In general, then, the transport and phototransport properties do not depend only on the nanoparticles diameter but also on their density and the morphology of the clusters that the particles form. These ideas and their experimental manifestations will be presented at the workshop.

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EQUILIBRIUM CARRIER TRANSPORT IN DISORDERED ORGANIC SEMICONDUCTORS

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It is shown that the charge carrier mobility in a positionally and energetically disordered hopping system can be evaluated by averaging either hopping rates or hopping times over the thermally equilibrium energy distribution of localized carriers. However, at variance with averaging hopping rates, averaging hopping times can be correct only if the energy dependence of the carrier energy relaxation time is also taken into consideration. The equilibrium carrier mobility was calculated by averaging hopping rates as a function of the temperature and concentration of localized sites. The obtained results prove that, in good quantitative agreement with both Monte Carlo simulations and experimental data, the temperature and concentration dependences of the mobility can be factorized, i.e. that the mobility can be represented as a product of two functions. The first function depends almost solely upon the temperature and reveals only a weak concentration dependence while the second one mainly governs the concentration dependence of the mobility and is almost independent of the temperature.

NEGATIVE MAGNETORESISTANCE AND ELECTRON-ELECTRON INTERACTION IN DISORDERED 2D MESOSCOPIC SYSTEM

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The transport on localized states is the main transport process in disordered systems. The scaling theory, which applies to non-interacting systems, shows that in 2D all the electronic states are localized for infinite systems. However, for mesoscopic systems this is true only whether the linear dimension of the sample L is larger than the localization length λ , which is not always the case. In addition, if a magnetic field is applied perpendicular to the plane, bands composed of delocalized states appear.

The transport is essentially influenced by coherence effects even when it occurs on localized states [1], so that the traditional Miller-Abrahams network formalism must at least be amended. The electron-electron interaction plays also an important role and even the Hartree approximation gives a significant contribution [2].

In this paper, we use a tight-binding model in which the localization is produced by trapping potentials distributed at random on the plaquette. The Landauer formalism is used for the calculation of the magnetoresistance in the regime of tunnel hopping between the bound states localized at the trapping sites. A negative magnetoresistance is expected at low magnetic field [3] and the main goal of the paper is to identify the effect of the Coulomb interaction of the localization and magnetoresistance.

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TRANSIENT AND METASTABLE PHOTODARKENING IN AMORPHOUS CHALCOGENIDES

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Transient photodarkening (PD), which is only observed during illumination, has been discovered in various amorphous chalcogenides. During illumination, total changes in absorption coefficient are a combination of transient and metastable part of PD and transient PD decays as the illumination is switched off to give the usually observed metastable PD. Till date most of the reported studies deal with the observation of PD after the illumination is switched off, i.e., the metastable PD.

The direct observation of transient PD was performed in a-As₂Se₃, a-As₂S₃ and a-Se thin films. Thin films were prepared onto Corning 7059 glass substrates by thermal evaporation in a vacuum of $\sim 2 \times 10^{-6}$ Torr at room temperature. a-As₂Se₃ and a-As₂S₃ films were annealed below their respective glass transition temperatures for 2 h and a-Se was kept at room temperature for 24 h before placing them in an evacuated cryostat for the measurements of optical transmission at various temperatures. Two laser beams were used: Ar ion laser ($h\nu=2.41$ eV and spot size 5 mm) was used as the action light (for inducing changes in absorption coefficient) and He-Ne laser ($h\nu=1.95$ eV, power < 1 mW/cm² and spot size 0.5 mm) was used as the probe light. The two lasers were made to cross each other at the sample. The transmitted signal of the He-Ne laser was made incident on a photo-diode and the changes in the transmitted light were measured with time. We define the changes in transmission as $\Delta T (=T/T_0)$, where T_0 is the transmission when the illumination is switched on and T is the transmission at any finite time t . No interference from the Ar laser was allowed on the photo-diode by using proper filters.

For a-As₂Se₃, a-As₂S₃ films, during illumination, total changes in absorption coefficient ($\Delta\alpha$) are a combination of transient and metastable part of PD. The transient part decays and reaches the usually observed metastable state on ceasing the illumination. The decay of the transient part of PD is explained well by a stretched exponential function. The magnitude of the transient part is surprisingly large especially at low temperatures. For a-Se, a large transient part of PD is observed at room temperature. After putting off the illumination, transient PD for a-Se decays and the changes in absorption coefficient reach the initial value (value before illumination). This is the reason for not observing metastable PD at room temperature for a-Se.

TRANSIENT PHOTOCURRENT TECHNIQUES AS A MEANS OF CHARACTERISING AMORPHOUS SEMICONDUCTORS

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We describes techniques to study electronic transport and localized state distributions in amorphous semiconductors from their photocurrent response to steady and impulse excitation. The response to impulse excitation contains information on distributions of trapping and release times for localized states in the mobility gap of the material; the problem is to determine a unique density of states (DOS) from such data. One technique is applicable to cases in which both trapping and release processes are significant. A second "post - transit" analytical is restricted to situations where only carrier release processes are significant. In both cases we derive analytical DOS spectroscopies capable of fine energy resolution. We also report on studies of transport and DOS distributions, in thin films of several representative chalcogenides, including recent studies of surface defect states in CdSe nanocrystals in SiO_x matrix. We also report on interpretation of steady state and transient measurements on thin film amorphous As₂Se₃.

DYNAMICS OF Ge-Se GLASSES AT STIFFNESS TRANSITION

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Nobody doubts the importance of glassy materials for daily life. However, we do not have quantitative theory even for understanding the window (silicate) glass, which is the central to ceramics, although Kingery [1] has given an excellent qualitative guidance. Here, firstly we demonstrate how the constraint theory of network glasses succeeds in describing the critical changes of crystallization tendency, fractal behavior and fragility at stiffness transition in the typical covalent chalcogenide glasses, $\text{Ge}_x\text{Se}_{1-x}$, using Raman scattering technique. Further-more, We discuss the physical nature beyond the description of the elegant constraint counting theory upon the dynamics at the Stiffness transition.

The mean coordination number $\langle r \rangle$ increases continuously with x to lead the stiffness transition at $\langle r \rangle = 2.4$ ($x = 0.20$) where the floppy (underconstrained) glasses become rigid (overconstrained) ones. Recently, Boolchand et al. [2] reported a transition window that an onset point of the transition near $\langle r \rangle_{(1)} = 2.4$ and a completion point at $\langle r \rangle_{(2)} = 2.46$. Thereafter, several computing results suggest that a self-organization associated with mechanism to understand the multiple transitions.

Investigating the temperature dependence of Raman spectra by heating the melt-quenched films from room temperature to 1000K, we find out a gap of crystallization tendency at the stiffness transition. On one hand, for $x < 0.04$ in $\text{Ge}_x\text{Se}_{1-x}$, as the small amount of $\text{GeSe}_{4/2}$ tetrahedra fails to prevent the crystallization of Se, mixtures of crystalline (-c) Se and liquid $\text{Ge}_x\text{Se}_{1-x}$ appear between the liquid and super-cooled liquid states. On the other, for $x > 0.18$, the large amount of $\text{GeSe}_{4/2}$ tetrahedra builds a medium-range structure topologically similar to the layered c- GeSe_2 to promote the crystallization of GeSe_2 . Embryo of c- GeSe_2 constructs in the super cooled liquid for $x > 0.10$, however, only those of $x > 0.18$ evolve into nuclei and crystallize. The transition of crystallization ability around $x = 0.18$ (note it is less than 0.20, the transition threshold), due to the connectivity of network, should be treated as an evidence of the stiffness transition.

We have found that a quasielastic contribution ($10\text{-}80\text{cm}^{-1}$) appears in the glasses of $x < 0.23$. While, for x not less than 0.23, the glasses crystallize without the appearance of the relaxational modes when we increase temperature. The composition dependence of the quasielastic intensity is well explained by the constraint counting theory under the assumption that the origin of the relaxational modes is from the floppy modes. We attribute the relaxation modes mainly to the damping or jumping motions of the rotating Se_n segments.

Between the Boson peak and relaxation contribution of the network, a valley at $3\text{-}10\text{cm}^{-1}$ is observed. The intensity ratio of the valley to the Boson peak is qualitatively regarded as the degree of the fragility. When the glass changes from floppy to rigid structure, the rapid drop of the intensity ratio points out a discontinuity of the fragility. The quasi-first-order transition suggests that the floppy-mode, related to the Se_n chains, exists in the underconstrained and disappears in the overconstrained glasses, since the fragility reflects the macroscopic properties of the network, mainly determined by the backbone structure.

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ION TRANSPORT IN CHALCOGENIDE GLASSES: DYNAMICS AND STRUCTURAL STUDIES

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The ionic mobility in glasses is at the origin of many applications in various domains (ion-exchange strengthening, chemical (micro)sensors, solid state (micro)batteries for electrochemical storage of energy, waveguides for integrated optical devices...). Thus, the survey of ionic transport in glasses is a topic that interests the academic research as well that the glass industry.

The knowledge of mobile ion dynamics at a macroscopic scale as well as at an atomic level is a necessity to bring an answer to the essential question : how can one link together structure, dynamics of ions and macroscopic properties of glasses ? Only some partial answers have been proposed to date.

The objective of the talk will be to summarise the state of our knowledge using the results that our group has obtained during the last years while studying a family of fast ion conductive glasses, i. e. that of silver chalcogenide glasses.

The following points will be emphasised :

- i) Variation of the conductivity with the mobile cation content ($\sigma_{dc} \propto X_{(Ag)}$, mechanisms of conduction).
- ii) Dynamic of ions ($\sigma_{ac} \propto f$ (Hz) from few Hz to the IR frequencies).
- iii) Is there a relationship between the glass structure (medium range order) and the conduction properties ?

STRUCTURAL RAMAN STUDIES OF Ge-BASED CHALCOGENIDE GLASSES

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The structure of binary $\text{Ge}_x\text{S}_{1-x}$ and ternary $\text{Ge}_x\text{Sb}_{0.4-x}\text{S}_{0.6}$ chalcogenide glasses has been investigated (for a variety of compositions) by measuring their Raman spectra, and discussed in terms of the structural atomic species present and of existing structural models. In addition to the ambient conditions measurements, the binary $\text{Ge}_x\text{S}_{1-x}$ alloys have been investigated under variable (i) high temperatures (up to temperatures above the respective melting points) and (ii) high pressures (up to 10.8 GPa), in order to detect any phase transitions or modifications of the structural units. In the ternary $\text{Ge}_x\text{Sb}_{0.4-x}\text{S}_{0.6}$ glasses, reversible and irreversible structural changes have been observed after various treatments of the samples including illumination by UV light or intense laser beam, and annealing below their glass transition temperature T_g .

It is well known that the network in $\text{Ge}_x\text{S}_{1-x}$ glasses consists mainly of $\text{Ge}-(\text{S}_{1/2})_4$ tetrahedra linked with each other via common corners or edges. The high temperature Raman measurements in $\text{Ge}_x\text{S}_{1-x}$ glasses show that, above T_g , irreversible phase transitions to crystalline phases occur for the compound GeS_2 ($x=1/3$) and the moderately rich in Ge ($x=0.35$) and S ($x=0.30$) glasses, but in the case of the strongly enriched in S ($x=0.20$) glass, the crystallization process is reversible with the material returning to its initial glassy phase upon cooling to room temperature. These phase transformations are discussed in terms of the dimensionality of the glassy networks involved in each case. The evolution with temperature of the A_1^c companion Raman band of the GeS_2 glass has provided support for the idea that this controversial band of the glassy phase is related to **symmetric stretch vibrations of S atoms in bridges of edge-sharing tetrahedra**. Raman scattering measurements above melting point have shown the existence of tetrahedral $\text{Ge}-(\text{S}_{1/2})_4$ units in the melts of some alloys, at least up to a certain temperature. The pressure dependence of the Raman bands of GeS_2 glass indicates that the Ge-S bond length decreases substantially with increasing pressure, while the material remains glassy throughout the pressure range. Above 10 GPa, GeS_2 glass becomes almost opaque, thus indicating a strong red shift of the absorption edge. All the pressure induced effects are reversible upon bringing the material to ambient pressure.

The observed Raman bands in the $\text{Ge}_x\text{Sb}_{0.4-x}\text{S}_{0.6}$ glasses are attributed to heteropolar M-S ($\text{M}=\text{Ge}, \text{Sb}$) bonds in the $\text{Ge}-(\text{S}_{1/2})_4$ tetrahedra and $\text{Sb}-(\text{S}_{1/2}\text{S})_3$ pyramids, as well as homopolar (defective) M-M bonds whose population increases with increasing Ge-content. Illumination by UV light or annealing below T_g of Ge-rich ternary glassy layers induces photostructural changes, the most prominent of which being an increase of the relative population of M-M to M-S bonds. Appropriate combination of the two treatments results in reversible structural effects. At higher intensities of illumination (by laser beam), partial crystallization of Sb occurs in both layer and bulk ternary glasses, with this effect being, again, stronger in the case of Ge-rich compositions. The extent of these effects is discussed in terms of the defective bond population, the free volume and the dimensionality of the glassy network.

INVESTIGATION OF PHOTOINDUCED EFFECT IN GaGeS BASED GLASSES AND THIN FILMS

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In this work, we will present the photoexpansion effect observed in GaGeS glasses when exposed to above band gap light (3.52 eV). A volume change of about 5% is reached in bulk sample by controlling time exposure and power density. Thin film have been also prepared by thermal evaporation from the glass compositions. In this case, a volume change of 25% is obtained under irradiation with bandgap (UV) light. The exposed areas have been analyzed using atomic force microscopy (AFM) and the optical absorption edge measured by spectrophotometer indicates a blue shift (80 nm) before and after illumination for composition $\text{Ga}_{10}\text{Ge}_{25}\text{S}_{65}$. The morphology was examined using a scanning electron microscope (SEM). The chemical compositions measured using a energy dispersive analyzer (EDX) indicate an increase of the sulfurs atoms into the irradiated area.

In order to evaluate the photostructural change, Extend X-Ray Absorption Fine Structure (EXAFS) has been performed. EXAFS spectra have been recorded in the Ge and Ga K edges for glass samples before and after illumination. Analysis of the EXAFS spectra show a intensity decrease of the Fourier transform first peak (Ga-S and Ge-S first coordination shell). This decrease indicates that a more disordered network is produced by light exposition. Otherwise, minor structural effects were observed at atoms located at higher distances.

LIGHT-STIMULATED STRUCTURAL TRANSFORMATIONS AND OPTICAL RECORDING IN AMORPHOUS NANOLAYERED STRUCTURES

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Light-stimulated structural transformations (LST) within the amorphous phase are well known in As_2S_3 -type bulk glasses and layers [1,2]. LST are used for the explanation of the attendant variations of the refractive index, optical transmission and some other physical and chemical parameters, including volume (thickness) change in homogeneous, thick layers. Therefore, these materials are suitable for optical recording of amplitude-phase image relief, which may be amplified or transformed into the surface geometrical relief after a selective etching.

Investigations of LST were extended towards the nanometer-thick layers and periodical, nanolayered structures [3,4] with the purpose to determine the influence of size-confinement on the structural stability and optical recording process.

In our experiments amorphous nanolayered structures (NL) similar to the compositionally modulated superlattices were prepared from a-Se and As-S(S, Te)-type chalcogenide glasses by the method of cyclic thermal evaporation in vacuum. The modulation periods were within the 5-12 nm range. High quality sapphire, Si or silica glass substrata and the developed deposition regimes as well, ensured good periodicity and interfaces in NL, that was proved by low-angle X-ray diffraction method.

Besides the observed build-in changes due to the nanometer dimensions (blue shift of the optical absorption edge in as-deposited NL), optical parameters (absorption, refraction and reflection) can be changed by laser illumination (usually at $\lambda=632$ nm) or by thermal annealing in a way different from the homogeneous thick layers. Additional peculiarities of optical recording and thermal erasing processes were connected to the light- or thermo-stimulated interdiffusion in NL. A model of this process was developed emphasising the role of the nanostructurization in the intermixing of adjacent layers. This model was extended also to the a-Si/Ge NL [5], where the thermally activated processes are dominant under the focused laser beam influence.

Giant light-stimulated extension was found in a-Se/ As_2S_3 NL and used for surface-relief production in a real time scale, without etching. Thus, optical recording due to the LST and interdiffusion can be applied for amplitude-phase optical elements' production with surface relief up to 180 nm, which are stable at room temperatures.

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APPLICATIONS OF CHALCOGENIDE GLASS OPTICAL FIBERS AT NRL

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Chalcogenide glass fibers based on sulphide, selenide, telluride and their rare earth doped compositions are being actively pursued at the Naval Research Laboratory (NRL). Great strides have been made in reducing optical losses using improved chemical purification and glass fabrication techniques, but further improvements are needed in both purification and fiberization technology to attain the theoretical optical losses. Despite this, current singlemode and multimode chalcogenide glass fibers are enabling numerous applications.

The authors will describe the glass compositions, chemical and glass purification processes as well as the fiberization techniques. The typical optical losses will be described along with the estimates of the theoretical losses and known mechanical properties. We will then discuss the applications of chalcogenide glass fibers. Examples include biomedical surgery, tissue/cancer diagnostics, chemical spectroscopy for environmental pollution monitoring, scanning near field IR microscopy and spectroscopy with sub-diffraction limit resolution for characterizing inorganic and biomedical samples; rare earth doped fiber IR sources/lasers for spectroscopy; amplifiers and optical switches for telecom applications.

The authors believe that the research and development of chalcogenide glasses will grow in the foreseeable future, especially with respect to improvements in the optical quality of the fibers and the performance of the fibers in existing and future applications.

ENGINEERING CHALCOGENIDE GLASS MATERIALS FOR INTEGRATED OPTICS APPLICATIONS

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Chalcogenide glasses (ChG's) have linear and nonlinear optical properties that make them attractive for use in integrated optics applications. Recent efforts in our group [1-10] to understand the changes in physical properties which accompany the use of ChG's in single and multilayer film structures, and subsequent aging behavior which would limit long term stability of such devices, are presented. These structure-property studies, coupled with device fabrication and component performance characterization, have resulted in an cohesive basis to analyze and evaluate attractive candidate glasses. The applicability of the resulting understanding towards realizing next generation optical components, is discussed.

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PHASE-CHANGE OPTICAL MEMORY PROMOTES THE DVD OPTICAL DISKS

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Crystalline-amorphous phase-change phenomena are accompanied by the change in optical constants of the material, as, e.g., the complex refractive index ($N = n + ik$) [1]. Chalcogenide thin film material in the system Ge-Sb-Te was investigated for rewritable optical disks. During laser irradiation, the film absorbs the energy, the temperature increases and the phase-change marks appear on the film, because the change of the optical constants give rises to the reflectivity changes.

The read-only optical disks, such as CD (compact disk), inscribe the information marks as pits on the polycarbonate injection mold substrate and the reflectivity is changed at the pit marks. The method of signal detection from the disk is the same both for the read-only CD disks and for phase-change rewritable disks: detection of the reflectivity changing. The disks show reading compatibility.

A big issue of write-erase cycle characteristics on phase-change optical disk emerged in early days of investigation. Authors [2,3] have succeeded breakthrough technologies on cycle issues and firstly realized overwritable phase-change optical disk products such as PD, CD-RW and rewritable DVD for the multimedia world.

The overwriting process of the phase-change optical disk memory includes melting by a pulsed laser spot and heating by the scanned laser spot. In the case of laser heat mode recording, the temperatures are rather high, over 600°C for the formation of the amorphous mark and 400°C for erasing of the mark by crystallization on the disk.

The fine grain ZnS-SiO₂ protection layer material, N₂-doped GeTe-Sb₂Te₃-Sb chalcogenide phase-change material and layer structure design, make breakthrough on cycle characteristics.

Thin substrate phase-change optical disk structure promoted high density 4.7 Gb DVD (Digital Versatile Disk) and rewritable DVD [4].

For high density recording, with laser optical means, only phase-change recording realizes dual-layer like a volumetric memory [5] and multi-level memory [6] wich increase the recording density. The combination of the technologies suggests the possibility to extend the recording density to more than 100 Gbit/inch².

In this paper I will discuss the interaction of the short pulse laser irradiation on the phase-change layer, compared to heat mode interaction.

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OPTICAL ACTUATION IN AMORPHOUS CHALCOGENIDES

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The opto-mechanical effect observed in amorphous chalcogenide films deposited onto clamped STM cantilevers [1] has been investigated. In this, bandgap light, incident on the chalcogenide film and linearly polarized either parallel or perpendicular to the cantilever axis, reversibly causes respectively either a contraction or an expansion of the chalcogenide layer, resulting in an optically-actuated displacement of the free end of the clamped cantilever. This effect is electronic, not thermal, in origin, and is believed to be caused by the same photo-induced structural rearrangements that are responsible for the optically induced optical anisotropy observed in chalcogenide glasses. Possible applications of this new all-optical actuation for optical switching will be discussed.

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STARTING MATERIALS PURIFICATION AND CHARACTERIZATION

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Various methods of synthesis and purification by zone melting, uniaxial solidification or recrystallization from solutions can be used to prepare starting materials for electronic or optical applications. Examples will be given of both preparation and characterization of such materials.

HIGH-PURITY GLASSES BASED ON ARSENIC CHALCOGENIDES

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The problems connected with the production and research of the properties of arsenic chalcogenides with low content of impurities are considered. The glasses of As-S, As-Se, As-S-Se, As-Se-Te systems have a number of interesting features making them promising optical materials. Many properties of the glasses, and most of all the optical properties, are sensitive to the presence of impurities. The data on the effect of impurities on glass properties are of great importance to fundamental and applied branches of science. The nature and the source of impurities are studied as well as the qualitative and quantitative aspects of their effect on glass properties. Carbon, oxygen, hydrogen, silicon are the limiting impurities chemically bound with the elements, being the macrocomponents of the glass, and with each other. The impurities, in the dissolved state or embedded into glass network, are the reason for the bands of selective absorption in the transmission spectra of glasses. Heterophase impurity inclusions of sub-micron size are a specific group of impurities. Their presence substantially effects the damage threshold and mechanical strength of glasses. The effect of impurities with selective absorption on the optical transparency of glasses can be detected with their content of 1-100 ppb depending on the nature of impurity.

Solidification of the melt of the glass-forming arsenic chalcogenide, synthesized by melting simple substances in the evacuated reactor of quartz glass, is the main method for production of optical grade chalcogenide glasses. The starting substances, the quartz container, and the residual vacuum gases are the sources of the impurities with selective absorption. Hydrogen income from quartz glass into chalcogenide melts was experimentally observed at 650°C and higher. Heterophase inclusions in chalcogenide glasses are the inclusions contained in the initial elements, and the non-dissolved reaction products produced as a result of the reaction between vapor and the chalcogenide melt with the reactor chalcogenides.

The paper considers the potentialities of different methods for production of high-purity arsenic chalcogenides and behavior of impurities in these processes. The content of impurities in the best glass samples is as follows: 0.5 ppm at. of hydrogen; 0.5-1 ppm wt. of oxygen and carbon; 0.5 ppm wt. of silicon; not more than $1 \cdot 10^4 \text{ cm}^{-3}$ of heterophase inclusions with the diameter of 0.08-0.1 μm . The experimental data are given on the effect of impurities on glass transparency at 1-11 μm as well as on the energy threshold of bulk damage under pulse radiation of YAG Er³⁺ laser.

CONTROL OF PHONON VIBRATION IN CHALCOGENIDE GLASSES FOR HIGH-PERFORMANCE 1.3 μm -WINDOW FIBER-OPTIC AMPLIFIERS

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Pr^{3+} and Dy^{3+} have been considered as promising active ions for 1.3 μm -window amplifiers for the fiber-optic communication. Large amount of research effort have been focused on the enhancement of the 1.3 μm emission properties of the $\text{Pr}^{3+}:^1\text{G}_4 \rightarrow ^3\text{H}_5$ transition. One of the major issues is to reduce the multiphonon relaxation from the upper emission level since the multiphonon relaxation seriously degrades the quantum efficiency of the transition. Non-oxide glasses, especially chalcogenides, can offer the potential to control the strong interaction between the rare-earths and host materials.

Current study concerns the control of the multiphonon relaxation by careful optimization of the local environment of rare-earths. Alkali halides were added to Ge-Ga-S glasses to modify the phonon vibration which directly affect the non-radiative transition in rare-earths. It has been observed that the addition of CsBr significantly increases the 1.3 μm emission intensity from both Pr^{3+} and Dy^{3+} . At the same time, lifetimes of the upper emission level increase as much as 40 times. Resistance to the crystallization upon re-heating is suppressed with the proper optimization of the host composition. Durability against the attack of liquid water will also be addressed.

CHALCOGENIDE GLASSES AS SENSITIVE MEMBRANES FOR THE DETECTION OF IONS IN SOLUTION

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In the last years the need for analytical devices to be used for environmental, industrial or medical controls has been growing up very quickly. Depending upon the concerned field two main requests can be noticed : 1) one for systems which could be used continuously on line and 2) one for miniaturised systems.

Chemical sensors based upon chalcogenide glasses are well adapted to the detection of chemical species in solution. They can reach the present needs for miniaturisation and in situ use since they are very durable in particular in neutral and acidic media and they can be easily shaped in thin films by the usual techniques of microelectronics. Moreover their very versatile composition allows the fabrication of specific membranes for many different types of ions (heavy metals such as Cu^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , anions such as S^{2-} , halide ions..).

Two examples of sensors based upon a vitreous chalcogenide ion-sensitive membrane will be given:

- First, an ion sensitive electrode (ISE) based upon a $\text{Cu}_x(\text{As}_2\text{S}_3)_{1-x}$ membrane has been prepared. It can be used for the detection of both Cu^{2+} ions and sulphide ones. The electrochemical characterisation of the ISE will be described. In both cases the ISE has a good detection limit (10^{-6} mol/l for either Cu^{2+} or sulphide ions) and a very good selectivity against interfering ions. Main interference comes from Fe^{3+} . Moreover this ISE can be used in a large pH range (3-10) which is especially interesting for the determination of sulphide ions in neutral or slightly acidic media (commercial electrodes work only at very basic pH). The ISE has been incorporated into an autonomous module allowing continuous in situ measurement of pH, temperature and sulphide content in solution. The module was tested for three months in water of thermal spring and the results validated against standard methods of sulphide titration.

- The second family of sensors is based upon a Cu-Ge-Sb-Se glassy membrane. In this case the sensors are miniaturised ones with the membrane being a sputtered film deposited from a composite target comprised of Cu metal and $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ glass. Two types of sensors, i. e. ISE and ISFET based one, were developed. The fabrication of both sensors and their electrochemical characterisation will be described. A limit of detection of about 10^{-6} mol/l and a very good selectivity against interfering ions (such as other heavy ions) are the main characteristics of these sensors.

OPTICAL AND MECHANICAL CHARACTERISTICS OF FIBERS MADE OF ARSENIC CHALCOGENIDES

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Optical and mechanical characteristics of optical fibers made of high-purity chalcogenide glasses of As-S, As-S-Se, As-Se and Ge-As-Se systems, intended for operation in the middle IR, are given. The fibers from As-S glass will be useful for transmission of IR-radiation in the 1-7 microns spectral region, the fibers on the basis of As-Se and Ge-As-Se glass systems - in the 2-12 microns region.

The techniques for manufacturing multi-mode, low-mode and single-mode fibers with low optical losses, based on the systems of the stated high-purity glasses, were developed. These are specially designed variants of the double crucible technique and of the «rod-in-tube» technique. They provide the given fiber parameters, i.e. the core-clad relation of diameters, thickness of primary and secondary coatings, core-clad concentricity and some other (about 10 reproducible) parameters. Depending on possible applications the fiber diameter can be changed from 200 up to 500 microns, diameter of the core - from 15 microns and more.

The multimode fibers from arsenic-sulfide and arsenic-selenide glasses have the minimum optical losses equal to 23 ± 8 dB/km and 79 ± 10 dB/km at 2.4 and 4.5 microns, respectively. The average bending strength of As-S glass fibers (with diameter of 350-400 microns) is from 1.0 up to 1.2 GPa, and from 0.4 up to 0.8 GPa for the fibers made of As-Se and Ge-As-Se glasses (at the rate of the plates drawing together being equal to 10 mm/min).

The single-mode fibers from As-S glasses have the minimum optical losses from 200 up to 400 dB/km in the 1.3 - 3 microns wavelength region.

The optical losses in multimode fibers at laser wavelengths are as follows:

from 0.17 up to 0.30 dB/m at YAG:Er-laser wavelength ($\lambda = 2.94$ micron) for the fibers made of As-S and Ge-As-Se glasses;

from 0.1 up to 0.3 dB/m at CO-laser wavelength ($\lambda = 5.5$ micron) - for the fibers made of As-Se glasses;

from 2.5 up to 5.0 dB/m at CO₂-laser wavelength (10.6 microns) for the fibers made of Ge-As-Se and Ge-As-Se-Te-glasses.

The choice of the glasses compositions for the fiber core and reflecting cladding which provides the given numerical aperture and the mode parameters in the required spectral region is discussed.

The features of modal distribution of radiation along the arsenic-sulfide fiber length were explored.

CHALCOGENIDE GLASSES FOR OPTOELECTRONICS

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While silica glasses are suitable for most optical applications there has been a growing interest in new special glasses including chalcogenides. This research is motivated by possible applications of such glasses in middle and far infrared spectral region (beyond $2\mu\text{m}$), due to their lower values of phonon energies and higher values of refraction indexes. For a long time these glasses have been studied for passive devices and optical fibres for laser power delivery but at present these glasses are attractive also for active devices that can be obtained by doping with rare earth ions (RE^{3+}). RE doped chalcogenide glasses possess fluorescence properties, far better than SiO_2 or fluoride glasses.

The attention is focused on the classification of these glasses - sulphide, selenide, telluride, and on the survey of their optical, physical and mechanical properties in comparison with silica, fluoride and heavy metal oxide glasses. The manufacturing of optical fibres implies a number of specific requirements. Ideally, the glass should comply with following requirements:

- stability against devitrification, in order to prevent crystallisation during fibre drawing
- intrinsic transparency at working wavelengths
- no (or very low concentration of) absorbing impurities
- no (or very low concentration of) defects and scattering centres
- durability in ambient atmosphere
- mechanical strength, thermal stability and insensitivity to ageing
- low cost and non toxicity

Glasses used for optical fibres should be free of absorbing impurities and scattering defects. Therefore, both anionic and cationic impurities must be controlled. This implies that starting materials are extremely pure and that processing does not induce any contamination. Physical defects include bubbles, crystals and insoluble species in the melt.

Basically chalcogenide glasses are synthesised in silica tubes or enclosures sealed under vacuum. As a result final glass contains all elements present in starting materials, including impurities. Because they are not stoichiometric, there is no concern for the control of the oxidation states. Contamination arises very easily, especially from water and oxygen traces. Preforms are made by rod-in-tube technique to avoid surface contamination.

This paper reports results on the preparation and characterisation of RE doped chalcogenide glasses. The main attention is focused on As-S, As-Se, Ge-Ga-S, Ge-Ga-As-S, Ge-Se-Te, As-Se-Te systems. Glass characterisation encompasses visual and microscopic observation, X-ray diffraction and infrared absorption. Scattering losses were evaluated from the shape and the size of the light spot that may be observed on the screen when He-Ne laser beam passes through the vitreous sample. Scanning electron microscopy together with low-temperature photoluminescence spectroscopy have been used for more detailed analysis.

PHYSICAL PROPERTIES OF DOPED CHALCOGENIDE GLASSY SEMICONDUCTORS WHICH ARE GOVERNED BY THE INTERACTION OF NEGATIVE-U DEFECTS AND IMPURITY STATES"

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Previous investigations have been revealed that in doped chalcogenide glassy semiconductors (CGS) a strong interaction of negative-U centers and impurity centers takes place. This interaction has both statistical and direct quantum-mechanical character. The latter has a result in a correlation between energies of negative-U centers and impurity states. The main result of the statistical interaction is so-called self-compensation processes which happen in time of doping treatment. Due to self-compensation processes a concentration of negative-U centers (D) is approximately equal to concentration of electrically active impurity centers (N).

The present paper is devoted to consideration of physical properties of doped chalcogenide glassy semiconductors which are governed by different relationship between D and N ($D \geq N$ or $N \geq D$).

First of all it will be discussed how relationship between D and N manifests in theoretical temperature dependence of direct current conductivity. Then we will discuss the experimental temperature dependence of direct current conductivity in CGS doped with transitional metals and temperature dependence of drift mobility in CGS doped with metals and halogens.

The last part of the paper concerns with the case when concentration of negative-U centers is enough to create band-like states. Possible superconductivity of this system is considered theoretically. The experimental data on mixture of doped selenium with micro-crystalline particles of high temperature superconductors is discussed.

EFFECTIVE HOLOGRAPHIC RECORD ON THIN FILMS OF CHALCOGENIDE SEMICONDUCTORS

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In this work the results of research thin films of chalcogenide semiconductors as materials for creation of relief holograms are submitted. The purpose was the optimization of these recording materials as photoresists.

Photoresist composition on which almost thousandfold chemical amplification of holographic record is achieved, was chosen. The value of the diffraction efficiency was changed from 0.02% before to 18 % after chemical etching. The optimization of photoresist has allowed receiving an essential rise in sensitivity to light, to expand area of effective spectral sensitivity in the region to shorter wavelengths. Diffraction gratings with greater spatial frequency can be obtained. In the work are shown the results on diffraction efficiency of reflective holographic diffraction gratings in a range of spatial frequencies 600 - 2400 grooves per mm. Samples of size 200×200 mm are experimentally received at exposure not exceeding $0.01 - 0.03 \text{ J/cm}^2$. For natural light the magnitude of the diffraction efficiency in the first order exceeds 70 % at measurements in autocollimator conditions.

Peculiarity of such materials is the increase of their sensitivity when exposed to short pulses. The exposure was carried out with single pulses of duration 40 ns on laser wavelength $0.53 \mu\text{m}$. The wide range of spatial frequencies was investigated. Diffraction efficiency equal 45 % was received on reflective holographic diffraction gratings in the first diffraction order at exposures $3 \times 10^{-3} \text{ J/cm}^2$.

In the paper the probable cause of distinctions between continuous and pulse influence of optical radiation on thin films of chalcogenide semiconductors is discussed. For this purpose the experimental data showing of a competition of processes of record and deleting at exposure are used.

The results of this work show the efficiency of the investigated photoresists used for the creation of holographic elements with various functional purposes. Some possible applications are discussed.

RADIATION DEFECTS IN AMORPHOUS As-Ge-S STUDIED BY POSITRON ANNIHILATION TECHNIQUES

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Characterization and identification of coordination defects is actual problem in the physics of chalcogenide glasses.

The microstructural origin of radiation-induced defects formation processes in amorphous Ge-As-S semiconductors, prepared by a standard melt quenching method, were investigated for the first time using the combined methods of IR Fourier spectroscopy and positron annihilation lifetimes measurements.

The radiation treatment of the investigated samples was performed in the normal conditions of the stationary radiation field, created in the closed cylindrical cavity owing to the concentrically established ^{60}Co ($E=1.25$ MeV) sources. The accumulated doses of $1\div 5$ MGy were chosen taking into account our previous results of radiation-induced effects investigations in the binary As-based chalcogenides [1]. The positron lifetimes measurements were carried out with an ORTEC spectrometer (^{22}Na isotope with 0.74 MBq activity).

The whole variety of the statistically possible coordination defects formation processes, associated with covalent chemical bonds switchings in the ternary As-Ge-S glass system, were analyzed. The pairs of diamagnetic over-coordinated positively-charged (As_4^+ , S_3^+) and under-coordinated negatively-charged (Ge_3^- , As_2^- , S_1^-) defects (the subscript - coordination number, the superscript - electrical charge excess) were supposed to be formed as a result of these transformations. The physically possible defects formation variants were selected and then put in the ground of the developed topological model for the observed radiation-structural changes.

This conclusion was confirmed entirely by positron lifetimes measurements. It was shown that only lone average lifetime (near 0.35 ns) was proper to the non-irradiated glasses corresponded to low concentration of negatively-charged coordination defects. Two different lifetime components in γ -irradiated samples were observed, the long-living one at the level of 0.38 ns being attributed to positron annihilation on As- and Ge-based defects and the short-living one (near 0.28 ns) - on S-based defects in good agreement with previous experimental data [2].

The compositional dependences of the investigated coordination defects formation processes in the above chalcogenide semiconductors were treated in the terms of average coordination number and "free" volume concepts.

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ATOMIC AND ELECTRONIC STRUCTURES OF GLASSY $\text{Ge}_x\text{Se}_{1-x}$ AROUND THE STIFFNESS THRESHOLD COMPOSITION

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For non-crystalline covalent networks constrained by bond-stretching and bond-bending forces, the covalent bonding may be optimized when the number of constraints equals the number of degrees of freedom [1]. Then a rigidity percolation takes place as the average coordination number $\langle r \rangle$ of the system passes through the threshold value of 2.4 [2]. During the last two decades, the prediction of this rigidity percolation has stimulated a number of experimental works on glassy (g-) $\text{Ge}_x\text{Se}_{1-x}$ alloys as a prototype system, such as Raman scattering, modulated differential scanning calorimetry, molar volume, and Mössbauer spectroscopy [3]. Despite such intensive work on this interesting system, there is no study that explores the precise concentration variation of the atomic and electronic structures. In this paper, I would like to review our anomalous X-ray scattering (AXS) [4] and ultraviolet photoemission/inverse-photoemission spectroscopy (UPS and IPES) [5] experiments on g- $\text{Ge}_x\text{Se}_{1-x}$ around the stiffness threshold composition.

For studying the atomic structure, AXS experiments were performed at two energies below the K edge (-15 and -200 eV) of each element using a θ - 2θ diffractometer installed at the beamline BM02 of the ESRF. From the total structure factor $S(Q)$, it was found that only the prepeak around 10 nm^{-1} indicates a strong concentration variation around $x = 0.2$ in its Q position and intensity. This suggests that the intermediate range order changes due to the rigidity percolation. From the detailed analyses of the AXS spectra, it was found that only the differential structure factor close to the Ge K edge, $\alpha\text{Ge } S(Q)$, shows a prominent prepeak, while $\alpha\text{Se } S(Q)$ indicates almost no signal at the prepeak position. Thus, it appears plausible that the prepeak originates from Ge-Ge correlation in g-Ge-Se mixtures.

To test our idea that the percolation phenomenon should sensitively be reflected in the electronic states, the density of states in the valence and conduction bands were investigated using UPS and IPES techniques, respectively. Thin (5 nm) film samples were produced by evaporating the material onto freshly prepared Au substrates. Significant concentration changes from GeSe_2 -like to Se-like were found between $x = 0.20$ and 0.25 in the UPS spectra and between 0.18 and 0.20 in the IPES spectra. We believe that both the AXS and UPS/IPES results provide experimental evidence for the rigidity percolation threshold, much directly in comparison with those reported so far. For a further understanding of these findings, i.e., the relation of the intermediate atomic and electronic structures to the rigidity percolation in the g- $\text{Ge}_x\text{Se}_{1-x}$ system, molecular orbital calculations using model cluster structures based on our AXS results are now in progress.

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POLYMORPHIC-CRYSTALLOID STRUCTURE AND RELAXATION PROCESSES IN SOME CHALCOGENIDE GLASS-FORMING SUBSTANCES

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Vitreous substance is built from co-polymerized structural fragments of various polymorphous modifications (PMs) without a long-range order (crystalloids). The concept of crystalloid is related with the concept of the intermediate-range order (IRO) in the atomic arrangement in glass and crystal substance. The IRO is a stereometrically determined composition (topology) of short-range orders (SRO) in the crystalloid area which is characterized by parameters of these SROs and dihedral angles peculiar to PM which the given crystalloid belongs to. There are no less than two SROs and two IROs characterizing structures of various PMs.

The main physical-chemical essence of relaxation processes of glass-forming liquid and solid vitreous substance (viscosity alteration, vitrifying, stabilization, mono- and bi-variant crystallization, softening, etc.) is generation, inter-transformation and decay of crystalloids of various PMs, their co- or de-polymerization and alteration of concentration ratio which result is change of relaxing substance properties.

Cooling of melt below T_m enforces co-polymerization and simultaneously causes transformation of low-temperature PM (LTPM) unstable in this temperature range into crystalloids of high-temperature PM (HTPM). At the cooling rates lower than critical one (V_{cr}), all LTPMs crystalloids are transformed in HTPMs crystalloids and the melt is crystallized as HTPMs. At $V > V_{cr}$ the co-polymer of LTPM and HTPM crystalloids is gradually getting the viscosity of solid substance – it is vitrifying. Relaxation of substance at heating goes as follows.

At heating of crystal LTPM, its conversion in HTPM takes place: in the case of enantiotropic transformation (GeSe_2 , GeS_2 , AsSe) – immediately above the transformation temperature T_{tr} , in the case of monotropic transformation (Se) – with gradually increasing with temperature transformation rate V_{tr} .

At heating or annealing of glass obtained from enantiotropic substance, at $T < T_{tr}$ the process of transformation of HTPM crystalloids in LTPM crystalloids takes place with subsequent crystallization as LTPM. At heating of this glass transformation of LTPM crystalloids in HTPM crystalloids and de-polymerization of glass take place right above T_{tr} which are observed as the softening temperature T_g+ ($\approx 350\text{--}370^\circ\text{C}$ for GeSe_2 , 495°C for GeS_2 , $\approx 180^\circ\text{C}$ for AsSe) lying in the T_{tr} range. Further heating or annealing of glass leads to crystallization as HTPM with subsequent its melting.

At heating or annealing of glass obtained from substance with monotropic polymorphous transformation, the transformation rate of LTPM crystalloids in HTPM crystalloids increases gradually along with temperature increase. The most active stage of this transformation followed by active de-polymerization of substance is observed as T_g+ ($\approx 37^\circ\text{C}$ for Se). Then glass crystallization as HTPM takes place, and at subsequent heating - it melts.

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ELECTRICAL SWITCHING IN CHALCOGENIDE GLASSES- SOME NEWER INSIGHTS

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Ovshinsky has discovered the electrical switching in chalcogenide glasses, nearly about three decades ago. Though the promised applications in information storage or power control have not been fully realized, electrical switching has remained to be one of the most fascinating properties of these materials.

It is known for long that there is an intimate relation between switching voltages properties such as glass transition temperatures, the resistivities of the samples, etc. However, the recent experiments are the first to bring out the close relation between the electrical switching and structural effects in chalcogenide network glasses. The two Topological Thresholds, namely the Rigidity Percolation and the Chemical Threshold are found to influence considerably the composition dependence of the switching voltages of many memory and threshold switching glasses. Also, a change in the switching behavior (memory to threshold), due to a change in the coordination of constituent atoms, has been seen for the first time, in a ternary chalcogenide system. Further, an interesting relation between the thermal diffusivity of the material and the type of switching exhibited (memory or threshold) is brought out. It seems to exist a closer analogy between the electrical switching behavior and pressure induced metallization of glassy chalcogenides.

The present talk will highlight how these results provide some newer insights to the origin of switching in amorphous chalcogenides.

PHYSICAL AGEING IN CHALCOGENIDE GLASSES

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Thirty year ago, the first sentence of a paper devoted to glassy chalcogenide based materials was as an example:

"Chalcogenide glasses exhibit many useful electrical optoelectrical threshold and memory switching properties and thus appear as good candidates for new technological applications".

Today, basically the same sentence is used and in spite of all these useful properties, it seems that all these hopes were not followed by concrete applications. In fact, one of the most important behaviour of a glassy structure is often omitted.

By definition, a glass is characterised by a lack of thermodynamic equilibrium. As a consequence, all the physical properties are time dependent, which is generally refereed as physical ageing phenomenon.

What are the consequences of physical ageing on a given property? This key interrogation must be associated with a second one: do correlations exist between the glass structure and its physical ageing kinetic?

In this work from a review of results obtained on different vitreous chalcogenide systems, I show that some interesting tendencies can be found.

SPECTROSCOPIC STUDIES OF RARE-EARTH DOPED As_2S_3 GLASSES

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Glassy As_2S_3 is a promising candidate for optoelectronics applications because of its high transmission in the infrared (up to 10 μm), high refractive index (~ 2.5) and low phonon energy. Special interest for applications is connected with doping glassy As_2S_3 by optically active rare-earth and transition metal ions. Due to broad band tail absorption of the doped As_2S_3 glass, absorbed photon energy is transferred to dopant metal ions and this result in increasing pumping efficiency. This is an important effect for applications such as in fibre optics amplifiers for the 1.3 μm telecommunication window.

In the present report we study the effect of rare-earth (Dy, Sm) and transition (Mn) metal ion luminescent impurities on the structure and optical properties of As_2S_3 glass in a wide spectral region. For this purpose we have employed Raman, infrared, band-to-band reflectance and edge absorption spectroscopies. The effect of light-soaking and thermal treatment on doped As_2S_3 glasses was examined as well.

Glasses were prepared from As and S (6N) and dopant elements (5N) by conventional melting (850 $^{\circ}\text{C}$, 24 h), with the impurity concentration being 0.1 and 0.5 at.%. X-ray and DTA techniques verified the glassy nature of samples. Bulk samples ($d=2$ to 3 mm) and thin films ($d=2$ to 9 μm , prepared by flash vacuum evaporation) were used for optical measurements. Infrared reflectivity spectra were recorded on a Fourier-transform vacuum spectrometer in the range 50 to 5000 cm^{-1} with 2 cm^{-1} resolution. Optical constants n and k were calculated by Kramers-Kronig analysis of the reflectance data. Light soaking experiments of bulk and thin-film samples were performed in a SolarBox-1500 device.

The effect of metal ion doping on As_2S_3 glass was detectable in several parts of the spectrum, including electronic transitions in the fundamental and impurity-related energy intervals and vibrational modes. In the fundamental absorption region, a reflectivity maximum at 24,000 cm^{-1} (2.98 eV) shows blue (Dy, Sm) or red (Mn) shift depending on the electronegativity of the impurity ion, in accordance with the corresponding variations of glass structure. Near the edge absorption, the impurity affects strongly the slope and the magnitude of weak absorption tail. In the wide range of transparency, the impurity was found to suppress several absorption bands indicating interaction of dopants with the host glass contaminations. Some variations of Raman bands under light exposure and thermal aging of doped glasses were also revealed. The observed effects of dopants on the spectroscopic properties of As_2S_3 glass are discussed in connection with the expected behavior of impurities in glass, such as their influence on the interlayer distance.

IDEAS CONCERNING THE OBTAINMENT OF NON-CRYSTALLINE MATERIALS BY MELT UNDERCOOLING

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A short selective review of concepts and ideas concerning the conditions in which the melts may be undercooled in vitreous state is presented.

The classical rules concerning the glass formers and modifiers established for oxide glasses are remembered and their applicability to chalcogenide glasses are discussed. The glass forming condition based on the so-called kinetic barriers, delimiting the industrially utilizable melts suggests the existing correlation with their structure and with the chemical bond energy.

The important role of the cooling rate in the broadening of the glass forming domains, encouraging the appearance of new ultra high cooling rate techniques, is underlined.

New correlation data between the undercooling in the vitreous state tendency and the basicity is demonstrated. The industrial glasses have pB comprised between 50 and 63 %. The melts with greater pB values may be obtained in glassy state only by rapid cooling techniques.

The new evidenced fact that the classic glass formers are located in the central field of the basicity scales, i.e. approximately between 40 and 60 % of pB, is discussed.

The speed of the heat dissipation V_{hd} , as a very general glass forming condition, is defined. The fulfilling of this condition allows to get every liquid or melt in vitreous state. On the basis of V_{hd} it can be made a new classification of melts according to their undercooling tendency in the vitreous state.

The two new possibilities of melts undercooling tendency estimation can be easily used, the necessary data being accessible.

PHOTOELECTRET PROPERTIES AND HIGH-FIELD POLARIZATION IN CHALCOGENIDE GLASSES AND THIN FILMS

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The work is dedicated to the late Prof. R. Andreichin, the founder and the pioneer of the photoelectret state investigations in wide band-gap semiconducting glasses.

Prof. R. Andreichin had worked together with the discoverer of the photoelectret state (PES), Academician G. Nadjakov. Prof. R. Andreichin with co-workers from his laboratory studied in details PES in chalcogenide glasses. Thus, the first part of the work is supposed to be a short historical presentation. A short review on the matter of the photoelectret state will be given.

In the second part attention will be paid on different difficulties that met the researcher when investigating electrical properties of wide band-gap materials. Typical mistakes will be pointed. Several counsels regarding how to avoid these mistakes will be proposed.

A brief review of different opinions about the usability of the obtained results (including thermally stimulated depolarization) will be given.

The question about the reliability of the obtained results of electrical properties of wide-band gap semiconductors will be discussed.

In conclusion, results of chalcogenide glasses and thin films electrical investigations in ISSP will be summarized.

Abstracts of Poster Papers

DONOR - AND ACCEPTOR - LIKE CENTERS FROM PHOTOCONDUCTIVITY OF AMORPHOUS THIN FILMS OF As_2Se_3

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In this paper are reported the results on determination of the density of trap and photogeneration centers of a charge inside the forbidden gap of As_2Se_3 .

Thin amorphous layers of width about $1\ \mu\text{m}$ were obtained by thermal evaporation in vacuum on the glass substrates. There were obtained coplanar and sandwich structures such as $\text{Au}-\text{As}_2\text{Se}_3-\text{Au}$. The steady state transversal photoconduction (I_{ph}) was studied as a function of illumination (range of intensity ~ 6 orders $1.5 \times 10^{10} - 1.5 \times 10^{15}$ quanta/(cm^2s)) and temperature (286 - 413 °K). On a sandwich sample were carried out measurements of dependence on energy of the density of the localized state ($N(E)$) by the method of non-steady electrophotographic spectroscopy deep levels (NESDL). From temperature dependence of a photoconduction two types of centers were found: the donors at energy 1.05 eV and the acceptors at energy 0.76 eV (the energy is measured from the top of the valence band), which energy does not depend neither on intensity nor on photons energy of photogeneration (at $h\nu > 1.5$ eV). The estimation of the concentration of centers participating in photoconductivity was done. The problem of strong electron - phonon interaction of these centers is discussed.

The results obtained from measurements of photoconduction are in agreement with the results from literature reported for thick As_2Se_3 glassy samples.

On the other hand, the results obtained from measurements of the relaxation of photoconduction and from the method NESDL evidence the quasi-continuum distribution of electrical charge traps $N(E)$ in the whole forbidden gap of an amorphous semiconductor with maximum at 0.62, 0.87 and 1.06 eV.

ON THE STRUCTURE AND ELECTRICAL PROPERTIES OF CdSe THIN FILMS

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CdSe thin films ($d = 0.08 - 1.25\ \mu\text{m}$) were deposited on glass substrates by the quasi-closed volume technique, under various conditions: deposition at rates from 9 to $110\ \text{\AA/s}$, the substrate temperature between 290 and 400 K and the temperature of the evaporation source between 900 and 1050 K. AFM investigations showed that the films have a polycrystalline structure. The average size of the crystallites ranged between 20 nm and 100 nm and increases with increasing film thickness and substrate temperature during film deposition. A heat treatment performed after film deposition determines the increase of the crystallite size.

The temperature dependences of the electrical conductivity and Seebeck coefficient have been investigated. For heat treated samples the thermal activation energy of electrical conduction is $E_a = 0.15 - 0.25$ eV. In the temperature range 320 - 525 K the Seebeck coefficient was found to be negative for all samples and to increase with increasing temperature.

The values of some characteristic parameters (charge carrier concentrations, ratio of carrier mobilities, etc.) have been estimated from the temperature dependences of the electrical conductivity and Seebeck coefficient.

WAVEGUIDES BASED UPON CHALCOGENIDE GLASSES

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Interest in chalcogenide glasses for integrated optics has been growing during the past few years [1,2]. Indeed, their transparency in the infrared, their high refractive index and their well-known photosensitivity properties make them competitive materials for several technological applications related to detection in the IR spectral domain. Our present work is focused on two types of applications: spatial interferometry and optochemical sensors for environment metrology.

- As the detection of planets implies the use of components working in the far infrared, we are focusing on the possibility of integrating chalcogenide glasses in the realization of such components for astronomical interferometry applications. In this context, we are now investigating the possibility of fabrication of a monomode channel "all chalcogenide" waveguide. To date, only a multimode planar "all chalcogenide" waveguide has been fabricated. As shown in Figure 1, this waveguide was made by depositing three superposed chalcogenide thin layers on a polished chalcogenide bulk substrate. The external $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ glassy layers were obtained by RF-sputtering using a commercial target, while the inner $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ glassy film was obtained by thermal evaporation from the powdered bulk glass (prepared by the classical melt quenched method).

- The optochemical sensors we plan to fabricate are based upon the realization of single-mode chalcogenide rib waveguides. The final structure of the component to be obtained is presented in Figure 2. The $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ chalcogenide glass was chosen for having no absorption for energies below 2 eV and a relatively stable refraction index value at 2,33. The first part of our work has been to optimize the deposition parameters of glassy thin films onto a Si/SiO_2 substrate by RF-sputtering. Films with good adhesion and controlled composition are currently obtained. We are now focusing on the etching of these films. Several ways are being investigating (plasma etching and chemical etching using a mask).

Progress in our investigations is presented in the poster.

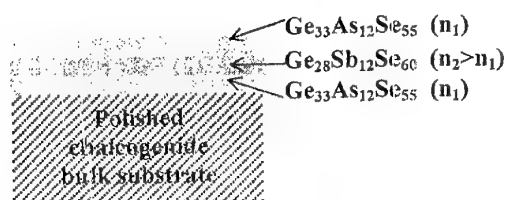


Fig. 1. Multimode planar « all chalcogenide » waveguide. The darker the grey, the higher the refractive index.

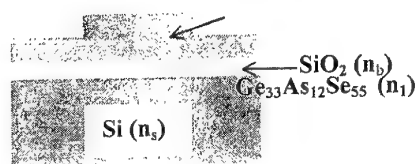


Fig. 2. Single-mode chalcogenide rib waveguide. The darker the grey, the higher the refractive index.

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NEW CHALCOGENIDE GLASSES IN THE $\text{GeSe}_2\text{-As}_2\text{Se}_3\text{-CdTe}$ SYSTEM

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During the last years the scientific interest towards chalcogenide glasses has been provoked by their properties and new application's possibilities. The interest is due to simple methods of their preparation in bulk and thin film form. Possibility for property variations is also a big advantage of the chalcogenide glasses.

Glassforming regions in $(\text{GeSe}_2)_x(\text{As}_2\text{Se}_3)_y(\text{CdTe})_z$ system, where $x+y+z=1$, have been determined. Glasses were investigated by visual, X-Ray diffraction and electron microscope analyses. Glass formation has been observed entirely along the tie-line $\text{GeSe}_2\text{-As}_2\text{Se}_3$ and partially along the lines $\text{As}_2\text{Se}_3\text{-CdTe}$ and $\text{GeSe}_2\text{-CdTe}$ (0-15 mol.% CdTe). Basic physico-chemical characteristics of the glasses were investigated – density, microhardness, transformation temperature, crystallization temperature, melting temperature. Transformation temperature (T_g) and melting temperature (T_m) are in the situated range 120-950 °C. X-ray diffractograms show two exo-effects observed at 440°C and 565 °C due to the crystallization of GeSe_2 and CdTe phases, respectively. The endo-effect examined at 680 ± 20 °C is connected to the melting temperature of solid solution $\text{GeSe}_2 + \text{As}_2\text{Se}_3$. The stability of the investigated chalcogenide glasses has been determined using the rule $\Delta t = T_g - T_m > 100$ °C. The calculated density values of the samples are between 4.36 and 4.58 g/cm³. The microhardness varies in the range 85-125 kgf/mm². The compositional dependence of these properties is discussed. Some thermal characteristics were obtained after differential thermal investigations of the glasses – elastic module (E), bonding energy (E_b), minimal volume of the microholes (V_h). The compositional dependence of the average coordination number is also presented.

HOMOGENEITY THRESHOLD IN SULPHUR RICH Ge-S GLASSES

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$\text{Ge}_x\text{S}_{1-x}$ glasses have been intensively studied for many years. Great effort was paid to the study of short-range order (SRO) in these materials. Several structural models have been proposed to describe SRO: random covalent network model (RCNM), chemically ordered network model (CONM) and Phillip's model. All these models were used by Lucovsky and coworkers [1] for interpretation of Raman spectra of Ge-S glasses with sulphur overstoichiometry. It was supposed that mostly two atoms of sulphur link Ge atoms and that the excess of sulphur separates as new phase. But these approach have led to discrepancy between computed and experimental data for increasing overstoichiometry of sulphur. Previously we have proposed SRO-model based on the assumption that the atom in excess of the stoichiometric composition of GeS_2 is considered to be the central atom of the respective structural units in the $\text{Ge}_x\text{S}_{1-x}$ system [2]. The structural units formed in the studied glasses are (Ge-S-Ge), (Ge-S-S) and (S-S-S). To test this SRO-model the Raman spectra of Ge-S glasses with sulphur overstoichiometry were studied with respect to compositional dependence of S_8 rings and polycathenasulphur S_n chains. Unfortunately the most intensive Raman band of S_n sulphur at 459 cm^{-1} is close to 475 cm^{-1} band of S_8 rings. To separate S_n and S_8 compositional dependencies of their intensities the compositional dependence of the well-resolved band of S_8 at 220 cm^{-1} was used. Raman spectra of studied glasses were measured for $x = 0.15, 0.20, 0.25, 0.30$ and 0.333 . It was found that the compositional dependence of the sulphur content (S_n chains and S_8 rings) is in agreement with theoretical prediction of SRO-model. Increasing concentration of S_n chains was found when the sulphur overstoichiometry increases from stoichiometric composition (GeS_2) and at the same time concentration of S_8 rings remains low. But when the sulphur overstoichiometry exceeds 77 at.% ($x = 0.23$) the concentration of S_8 rings increases rapidly and they can create separated phase. Structure of studied sulphur rich glasses can be imagined as GeS_4 tetrahedrons linked together with S_n chains and co-existing separated phase of cyclooctasulphur for $x < 0.23$. Based on this result we consider that $\text{Ge}_x\text{S}_{1-x}$ glasses are microheterogeneous for $x < 0.23$. Our homogeneity threshold at $x \sim 0.23$ corresponds with Boolchand's micro-Raman and MDSC measurement [3] of $\text{Ge}_x\text{Se}_{1-x}$ glasses. He found that near $x = 0.23$ (mean coordination number $\langle r \rangle = 2.46$, rigidity transition threshold) the structure of Ge-Se glasses changes from rigid to floppy one with increasing selenium content.

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THERMAL PROPERTIES OF As-S GLASSES IN THE GLASS TRANSITION REGION

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The glasses of the $\text{As}_x\text{S}_{(100-x)}$ system, where $x = 33 - 42$ at.%, were prepared by direct synthesis from the pure elements. The differential scanning calorimetry (DSC) experiments were performed using DSC Pyris 1 (Perkin-Elmer). The StepScan (Perkin-Elmer) method in the heating regime was used to separate thermodynamic C_p (fast reversible phenomenon) and kinetic (slow irreversible processes) components of the glass transition. The dependencies on As concentration of specific heat capacity difference, $\Delta C_{p,T_g}$, configurational entropy, ΔS_{T_g} , and Gibbs free energy, ΔG_{T_g} , were calculated over the glass forming region from measured specific heat capacity data. All obtained data were plotted as functions of the mean coordination number $\langle r \rangle$, too.

It was found that dependence of the glass transition temperature, T_g , on As content has a maximum for stoichiometric composition As_2S_3 . The dependence of $\Delta C_{p,T_g}$ on As content reaches maximal value for As_2S_3 , as well. The significant change of slope of $C_{p,g}$ (specific heat of glass at 140 °C) vs. mean coordination number, $\langle r \rangle$, for $\langle r \rangle \sim 2.35$ ($x \sim 35$ at.% of As) was observed. The dependence of $\Delta C_{p,T_g}$ on As content has the same shape for studied glasses as was found by Boolchand [1] for glasses of As-Se system. Strong changes of $\Delta C_{p,T_g}$, ΔS_{T_g} and ΔG_{T_g} vs. x in the 35 and 38 at.% region were also found. It can be caused by a change of structural units in these glasses which corresponds well with above mentioned change of slope of $C_{p,g}$ for $\langle r \rangle \sim 2.35$ ($x \sim 35$). For mean coordination number $\langle r \rangle = 2.4$ ($x = 0.40$, stoichiometric composition) the values of both $C_{p,g}$ and $\Delta C_{p,T_g}$ reach extremes. Borisova [2] assumed that when the As content raises in the range of 28 - 40 at.% the transformation of tetrahedral to trigonal coordination of the arsenic takes place and therefore glasses having compositions in the range from 33.3 to 37.0 at.% As are extremely sensitive to the heat treatment. Our experimental results have confirmed the Borisova's assumption and it seems clear that the structure of As-S glasses changes considerably depending on As content in the studied compositional region.

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STRUCTURAL CALCULATIONS FOR AMORPHOUS SYSTEMS USING STRUCTURAL DIFFUSION MODEL

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We present the results of calculations of the structure factor $S(k)$ and the pair distribution function $g(r)$ for amorphous nickel, cobalt and iron using Structural Diffusion Model (SDM) [1-2]. With the choice of local lattice structure made in this work, the agreement between the calculated and experimental $S(k)$ and $g(r)$ is reasonably good [3]. We suggest that the most promising procedure to choose the local lattice for SDM calculation of the amorphous systems studied in this work is to start with the fcc crystallographic unit cell.

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IRRADIATION INDUCED STRUCTURAL CHANGES IN $a\text{-Ge}_{20}\text{Se}_{80}$ GLASSY SYSTEM

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In the covalent network glass system $\text{Ge}_x\text{Se}_{1-x}$, the rigidity percolation threshold occurs at an average coordination number, $\langle r \rangle$, of 2.4, corresponding to $x=0.20$. Here we report Raman measurements on $\text{Ge}_{20}\text{Se}_{80}$ thin films before and after irradiation with white light and Kr^{++} ions. Bulk samples of amorphous $\text{Ge}_{20}\text{Se}_{80}$ are prepared by rapid cooling from the melt. Thin films are prepared by vacuum evaporation, onto 7059 Corning glass substrates. The composition of the films is found to be about $\text{Ge}_{21.5}\text{Se}_{78.5}$ by EPMA technique. Micro-Raman measurements are done on SPEX 1877E, using 514.5 nm line from an argon ion laser. Typical collection times are 300 s at a laser power 2 mW. All spectra are recorded under similar spectral parameters and analysed using the Gaussian Peak-Fit programme. Light soaking is done in vacuum using heat filtered white light (200 W tungsten lamp, 2500 lux) for 3.5 h. These films are irradiated at room temperature in vacuum ($\sim 10^{-6}$ torr) using 2×10^{13} ions/cm² fluence of 1 MeV Kr^{++} ion from a Van de Graaff Generator.

The bulk glass and its thin films show three Raman peaks at ≈ 200 , 215, and 263 cm^{-1} with small difference in the widths. Annealing the virgin films changes the widths but the positions do not change. The spectral features of the Raman spectra present in bulk, virgin and ion irradiated samples are assigned to the stretching mode of $\text{GeSe}_{4/2}$ corner sharing tetrahedra (200 cm^{-1}) and to the vibrations of Se atoms in four membered rings composed of edge sharing tetrahedra (215 cm^{-1}) respectively and a band near 263 cm^{-1} originating from Se-Se bonds [1].

Raman spectra after light soaking shows four bands instead of the three observed in the virgin and ion irradiated state. These are at 203, 221, 257 and 273 cm^{-1} . The bands at 203 and 221 cm^{-1} may be have the same origin as in the virgin state. The band at 257 cm^{-1} comes from the floppy segment of network, while the other (273 cm^{-1}) from the optimally constrained segment of the network [2].

In contrast, the number of peaks and their positions do not change after Kr^{++} ion irradiation. This shows that no new bonding configurations are created by ion irradiation. Also, ion irradiation increases the intensity of the vibrational mode at 263 cm^{-1} related to Se-Se bonds in chains. Light soaking, on the other hand, produces a new band at 257 cm^{-1} , which goes away after annealing the sample at 150 °C (2h). In addition, the width of 200 cm^{-1} band decreases after ion irradiation but increases upon light soaking. Our identification for the modes 257 cm^{-1} and 273 cm^{-1} is consistent with the observed widths of the mode, the one associated with the floppy phase is broader than the one associated with the optimally constrained phase. Results will be discussed on the basis of photomelting as suggested by Boolchand et al. [2].

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RESEARCH OF A MICROPLASMA BREAKDOWN IN THIN FILMS OF GLASSY SEMICONDUCTORS

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The analysis of electronic processes that occurs at high electric fields in thin films of glassy semiconductors is important both theoretically and practically. On the one hand theory of charge carrier multiplication in amorphous semiconductors continues to develop [1] and on the other hand there are various applications of chalcogenide films, for example, generating directed acoustic and electromagnetic radiation [2].

In the given work the outcomes of the experimental research of chalcogenide glassy semiconductors are presented. The purpose of the investigation was current instability that arises in a mode of "mild electrical breakdown". The measurements were fulfilled on samples of a different composition (Ge-Te, Ge-Se, Ge-Te-As and other systems). Samples of Al_2O_3 and SiO_2 were used as control ones. Pulse measurements included taking of voltage-current characteristics, breakdown voltage (at a given current), and currents at a pre-breakdown voltage. All measurements were performed in auto mode and the dataset contained 5000 points, with lag between points varying in a interval from 20 μs up to 100 ms. The data were processed by standard statistical methods: Fourier analysis, wavelet analysis, dispersion constructions, phase-space diagrams, lag plots, correlation diagrams etc.

The applied techniques have allowed finding out electrostress processes having different time constants and resulting into decrease of electric strength of the samples. The processes under consideration appear to be multistage and reversible since they don't depend on head effects on the initial state.

The obtained results were explained within the framework of the following model: in the initial stage of a breakdown, carriers injected from the metal produce contact barrier modification; then plasma channel emerges, which is thereafter accompanied by an electrical field reallocation; in the next stage, region of carrier multiplication grows with the subsequent development of a sparkover. According to estimations, the current of an elementary microplasma channel did not depend on the composition of the material and has the value about $10^{-11} - 10^{-10}$ A.

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STUDY OF NON- ISOTHERMAL KINETICS, ELECTRICAL AND OPTICAL PROPERTIES OF Ga-Se-Te FILMS"

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Ternary $\text{Ga}_x\text{Se}_{86-x}\text{Te}_{14}$ ($x=15$ and 36) were prepared in amorphous state by quenching technique for the compositions $x = 15$ and 16 . Results of differential scanning calorimetry (DSC) at different heating rates are reported and discussed. From the heating rate dependence of glass transition, crystallization onset and peak crystallization temperature values for the glass transition activation energy, E_t , and the crystallization activation energy, E_c , were evaluated. The average calculated values of E_t and E_c are 140.29 and 97.89 kJ/mol. respectively. Electrical conductivity of amorphous $\text{Ga}_x\text{Se}_{86-x}\text{Te}_{14}$ thin films with different thickness have been measured in the temperature range 300 - 360 K with the aim to see the effect of a metallic impurity. It is observed that the increase of conductivity by increasing activation energy and lowering the pre- exponential factor that the results are explained in terms of the hopping conduction.

The optical constants of these films were determined by transmission and reflection measurements at normal incidence in the spectral range of 500 - 800 nm. The refractive index has anomalous behavior in the spectral range 400 - 500 nm. The refractive index dispersion is fitted to a single oscillator model. The allowed optical transitions were found to be indirect.

P11

MIXED VALENCE AND ELECTRON HOPPING IN SPINEL CHALCOGENIDES

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The chalcogenides systems with mixed valence electronic structure show very interesting magnetic and interaction properties.

The system $\text{FeCr}_{2-2x}\text{In}_{2x}\text{S}_4$, where $x = 0.0, 0.05, 0.10, 0.15$ and 0.50 was investigated using magnetic and Mössbauer measurements, between 1.8 K and 400 K.

There are several relevant aspects:

- a non-cooperative (dynamic) Jahn-Teller effect for tetrahedrally coordinated bivalent iron;
- the simultaneous presence of Fe^{3+} and Fe^{2+} induced by indium substitutions;
- the magnetic transition temperature and the electron hopping process are strongly influenced by substitution amount.

The data were interpreted in terms of a complex magnetic structure and a new trend in magnetic materials was suggested.

STUDY OF CARRIER TYPE REVERSAL OF $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{58}$ AND $\text{Pb}_{20}\text{Ge}_y\text{Se}_{80-y}$ GLASSES BY THERMAL DIFFUSIVITY MEASUREMENT

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Carrier type reversal in semiconducting glass is an important problem. There are several reports on the thermal and electrical properties of these glasses. However very little information is presently available as the structure and transport properties of these glasses. This paper is an attempt to extract more information on these series of glasses. Over the past few years the photoacoustic technique has developed into a powerful tool for studying the optical and thermal properties of solids. We report here, thermal diffusivity of bulk $\text{Pb}_x\text{Ge}_{42-x}\text{Se}_{58}$ ($x=0-15$ at%) (I series) and $\text{Pb}_{20}\text{Ge}_y\text{Se}_{80-y}$ ($y=17-25$ at%) (II Series) homogeneous glasses. Laboratory built non resonant photoacoustic cell is used to measure thermal diffusivity. The thermal diffusion length and thermal diffusivity have been measured for both series of samples. At a particular composition the thermal diffusivity is found to be lowest and the carrier type reversal reported takes place at that composition. It can be clearly seen that an anomalous behaviour is observed in series I at 9 at.% of Pb and in II series at 21 at% of Ge where the composition shows a transition from p to n type conduction. The possible bonds in these series are Ge-Ge, Ge-Se, Pb-Se and Se-Se. In I series, the concentration of calculated covalent bonds of Ge-Se and Ge-Ge changes gradually with relative increase in Pb-Se ionic bond. But in series II, besides Pb-Se ionic bonds, the Se-Se bonds decreases and completely vanishes at $x=20$ at % of Ge. It is speculated that in the series II the disappearance of Se-Se homopolar bonds causes the electrical conduction changes from p to n type.

P13

RAMAN SPECTRA OF $\text{Ge}_x\text{As}_y\text{Se}_{100-x-y}$ GLASSES

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Earlier [1] we had studied some physical (elastic and optical) properties of bulk $\text{Ge}_x\text{As}_y\text{Se}_{100-x-y}$ ($0 \leq x \leq 30$, $10 \leq y \leq 40$) glasses. Analyzing the data in the frame of the known glass structure topological concepts we had revealed that two topological phase transitions might be occurred at the mean coordination number $\langle m \rangle_1 \approx 2.4 \div 2.51$ and $\langle m \rangle_2 \approx 2.78$ (for studied glasses $\langle m \rangle = 2.1 \div 3$). In this work the Raman spectra of the same $\text{Ge}_x\text{As}_y\text{Se}_{100-x-y}$ glasses have been studied. They were measured for reflected light beam at room temperature. The standard back-scattering geometry of measurement was used. The laser line 630 nm of 25 mW He-Ne laser was used as a light source. Scattered light was analyzed using DFS-24 spectrophotometer. There revealed three sets of glasses, qualitatively differing in their spectra shape. The structure type of studied glasses is dependent partially on mean coordination number. The alloys with $\langle m \rangle \approx 2.1 \div 2.4$ exhibit the polymeric structure based on Se_n chains, which are cross-linked by Ge and As atoms. The basic structural units of this group of glasses are $\text{SeSe}_{2/2}$, $\text{AsSe}_{3/2}$ and $\text{GeSe}_{4/2}$. The structure of second set glasses ($\langle m \rangle \approx 2.51 \div 2.78$) is derived from 2D Ge-based molecular clusters and As-rich structural fragments. Glassy $\text{Ge}_{27}\text{As}_{37}\text{Se}_{36}$ and $\text{Ge}_{30}\text{As}_{40}\text{Se}_{30}$ ($\langle m \rangle \approx 2.91 \div 3.00$) compose the third set of alloys with 3D network.

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CHARACTERIZING OF THE Sb_2O_3 THIN FILMS BY X-RAY SCATTERING

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Thin films of Sb_2O_3 have been prepared by thermal sputtering on a substrate of SiO_2 . The X-ray scattering experiment from the Sb_2O_3 films was performed using a reflectometer. It consists of an X-ray source, a curved multilayer monochromator on the incident beam side, a slit in front of the sample mounted on the center of the circle of the goniometer and two slits preceding the detector on a circle of the diffracted beam side. Specular X-ray scattering is sensitive normal to the sample surface. It provides vertical structural structure parameters (the density and roughness of the glass and the density, thickness and roughness of the Sb_2O_3 layers on top of the SiO_2 substrate). The scanning of the surface was done at an incidence angle of the X-ray in the range of $0-12^\circ$ and the reflected intensity was recorded. The specular and diffuse X-ray scattering obtained from the deposited thin films, having various thickness, represent a method that is sensitive to density contrasts and can therefore be applied to all sorts of unpatterned surfaces and layered structures. It is applicable to structures on the nanometer scale and roughnesses on the subnanometer scale. The obtained data have shown that at least ultrathin Sb_2O_3 layers reveals a graded layer structure. The results can be used in controlling of the thin layers fabrication, particularly thickness determination that have to rely upon densities and optical constant of layers.

P15

VISIBLE LIGHT EMISSION FROM $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ NANOCRYSTALS

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Recently, there have been performed researches on the doped nanocrystalline semiconductors like ZnS:Mn or CdS:Mn . The d-electronic states of the Mn^{2+} ions act as the luminescence centers emitting in the green part of the visible spectrum; the efficiency increases by interaction with s-p states of the host nanocrystal.

In our work, luminescent emission, optical absorption and excitation spectra of some $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ nanocrystals have been measured at room and liquid nitrogen temperature. The Mn^{2+} ions give rise to a broad emission band centered at about 580 nm, between the emission bands of CdS host.

X-RAY EXCITED LUMINESCENCE AND X-RAY IRRADIATION EFFECT ON CdS_{1-x}Se_x NANOCRYSTALS OPTICAL ABSORPTION

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Photoluminescence (PL) of II–VI nanocrystals embedded in glass matrices is extensively studied in the recent years, providing, along with other optical techniques (absorption, Raman scattering) important information on the nanocrystal parameters. PL spectra are known to be essentially dependent on the excitation energy and power, therefore it seems interesting to investigate X-ray excited luminescence (XL) as well as take into account the luminescent properties of the glass matrix itself. Besides, it is important to study the effect of X-ray irradiation on the spectroscopic features related to quantum-size effects in II–VI nanocrystals.

We report the results of XL spectroscopic studies as well as the influence of X-ray irradiation (Mo anticathode tube, 40 kV, 20 mA) upon optical absorption spectra of CdS_{1-x}Se_x ($x=0.6$, $r=2.76$ nm and $x=0.78$, $r=3.08$ nm) quantum dots embedded in SiO₂–B₂O₃–ZnO–K₂O–Na₂O glass matrix.

In the XL spectra of CdS_{0.4}Se_{0.6} nanocrystals the bands at 2.04 and 2.36 eV are observed, while the spectrum of CdS_{0.22}Se_{0.78} samples consists of the bands at 1.92 and 2.21 eV, these results being compared with the PL studies. Note that XL measurements of borosilicate glass matrix itself enabled us to eliminate its contribution due to intrinsic and radiation-induced centres in glass.

The singularities related to the quantum-size levels, revealing as additional maxima in the non-irradiated CdS_{0.4}Se_{0.6} quantum dots optical absorption spectra, smear and vanish at the exposed dose D up to 540 Gy. Irradiation with up to 2700 Gy slightly shifts the absorption curve towards higher energies. In CdS_{0.22}Se_{0.78} nanocrystals the X-ray irradiation effect reveals not only in the maxima smearing, but also in the red shift of the second and higher quantum-size maxima with the irradiation dose increase. Note that in this case the maxima are still visible even at 2700 Gy.

Isochronal (20 min) annealing studies of the irradiated samples have shown the initial spectrum to recover below 560 K.

Two possible mechanisms of the observed effects related to the irradiation-induced ionization as well as the additional pressure on the nanocrystals from the glass matrix due to its radiation swelling, are discussed.

EFFECT OF PHOTO AND THERMAL DISSOLUTION OF Ag ON THE ELECTRICAL PROPERTIES OF a-As₂S₃

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The paper reports the measurements of electrical properties of As₂S₃ before and after photo / thermal dissolution of Ag into it. The samples in the form of pellets were prepared by compressing the finely grounded powder of a-As₂S₃. The dissolution of Ag into As₂S₃ was carried out separately on pellets by coating their faces with a thick layer of conducting Ag paste and thereafter subjecting them to two different treatments i.e. (i) optical, and (ii) thermal. A General Radio bridge (model 1620-A) was used for the measurements of frequency dependent a.c. conductivity and capacitance of the samples over a frequency range of 1 kHz to 100 kHz in the temperature range of 273 °K to 373 °K. The conductivity of As₂S₃ decreases with doping at lower temperatures. The a.c. conductivity is proportional to " ω^s " for undoped as well as for doped samples. The value of frequency exponent (s) decreases with increasing temperature, but increases with doping at same temperature. However, it has been observed, that in case of thermal doping, if the doping temperature is increased, the value of 's' also increases. The measurement of frequency dependence of dielectric constant 'k' at different temperatures indicates that at lower temperatures, the value of 'k' is the same for photodoped and undoped As₂S₃ whereas it is higher for thermal doped. At higher temperatures, the value of dielectric constant is maximum for photodoped As₂S₃, whereas the value of 'k' for undoped As₂S₃ does not vary much with temperature. A new structural model along with Correlated Barrier Hopping mode (CBH) [1-3] has been used to explain the effect of doping in the observed behaviour.

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P18

THERMO AND PHOTOLUMINESCENCE OF SILICATE LASER GLASS DOPED WITH NEODYMIUM

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The luminescence and thermoluminescence have been measured in vitreous materials doped with Nd³⁺. The luminescence spectra show a maximum at 400 nm and a shoulder at about 440 nm. The measured global thermoluminescence shows a broad band with a maximum at 270 °C which suggests a continuous distribution of electron traps induced by ionizing radiation. Thermoluminescence measured through two optical filters which transmit at about 400 nm and 440 nm wavelength shows a structured behavior with two glow peaks at 270 °C and 330 °C. This apparently contradictory behavior has been explained by the existence in this material of a continuous distribution of trap levels and a discrete distribution of recombination levels. The 270 °C and 330 °C glow peaks have been interpreted as being due to recombination of the electrons released from electron traps with O²⁻ and Nd³⁺ hole centers. Due to the high stability of the defects induced by the radiation observed from thermoluminescence measurements, this material could be used as a new radiation detector.

UV IRRADIATION EFFECTS IN PURE AND TIN-DOPED AMORPHOUS AsSe FILMS

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Pure and tin-doped AsSe amorphous thin films of thickness around 5 micrometer were investigated. The tin amount in films was ~10 at.%.

In order to search for structural differences between doped and undoped films, X-ray diffraction measurements at room temperatures have been performed on a Seiffert XRD-7 diffractometer equipped with a copper target tube.

The changes in the medium range order (MRO) of the films was followed by accurate profiling of the first sharp diffraction peak (FSDP) in the X-ray diffraction diagram. There was used a special procedure to eliminate the contribution of the silicon substrate to the diffraction pattern in the FSDP-region.

Then, the tin-doped film was irradiated with the radiation emitted by an ultraviolet medical lamp, with the emission-maximum at $\lambda=336$ nm and a power density of $116 \mu\text{W}/\text{cm}^2$. The structural changes induced by the irradiation were followed by X-ray diffraction.

Ten atomic percent of tin added to the basic AsSe composition determines significant transformations that includes a shift of the FSDP towards higher quasiperiodic spacings (from 5.45 Å in pure AsSe film to 5.66 Å in tin-doped film). Moreover, the width of the FSDP increases, which fact speaks in favour of more disorder induced by tin in the amorphous AsSe network.

The UV irradiation determines only a small shift of the FSDP towards higher quasiperiodic spacings ($d=5.70$ Å) and an additional broadening.

The structure of the tin-doped AsSe films was explained in the frame of a model with random insertion of Sn in the As-Se layers. The effect of UV-irradiation was interpreted by more disorder introduced in the atomic scale configurations by partial elimination of Sn-As direct bonds, and allowing for direct As-As bonds. This transformation under excitation is possible on the basis of the small bond energy differences between the two types of wrong bonds possible to exist in the not annealed structure, characteristic to fresh amorphous films (As-As bond energy is 46 kcal/mol, while Sn-As bond energy is 42 kcal/mol).

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MnS AND CdS CLUSTERS ENCAPSULATED IN NATURAL ZEOLITES

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The zeolite structures permit one to vary the cluster concentration, and the intercluster geometry in a controlled manner over the periodicity defined by the host zeolite lattice. The clinoptilolite structure (CLI) is characterized by large, intersecting open channels of eight- and ten-membered tetrahedral rings (7.05×4.25 Å respectively 4.60×3.95 Å). The laumontite structure (LAU) is characterized by channels of ten - membered tetrahedral rings (4.6×6.4 Å) which are parallel to [100] axes.

In order to remove the impurities, the powdered clinoptilolite, from Mârsid- Romania, was submitted to an acid treatment, using 1N HCl solutions. The laumontite monocrystals, from Stanija-Romania, were clear. The zeolites in their sodium cation form were first ion-exchanged to the Mn^{2+} and Cd^{2+} form, by treating with 0.1 N aqueous manganese or cadmium nitrate solutions at 296K and $pH = 5.5-5.8$. This was followed by the treatment with 1 molar solution Na_2S . The atomic absorption method evidenced a S/Mn ratio of 1.1 and a S/Cd ratio of 3.51.

The optical absorption spectra were obtained using a SPECORD UV/VIS spectrophotometer in the wavelength range 300-800 nm. Luminiscence spectra were also obtained at room and liquid-nitrogen temperature with pulsed excitation ($\lambda = 337.1$ nm, $\nu = 72$ Hz, $\tau = 10^{-8}$ s, 1.6 kW). Measurements of the electric resistance were made by means of an experimental arrangement using a KEITHLEY 6517A instrument.

The optical absorption spectra give the quantization effect as the estimation of band gap. The S-S and Mn-Mn distances and atomic charges are responsible for the bandwidths. As the charge transfer from S^{2-} to Mn^{2+} exceeds 0.4 the bandwidth becomes narrow (3.81 eV for the bulk β -MnS, 5.39 eV for MnS clusters in laumontite). In Clinoptilolite the p-d hybridization leads to a gap close to 2.28 eV. The absorption edge changes as a function of cluster-cluster contact distance in the zeolite (from 475 nm, for CLI-CdS, to 350 nm, for LAU-CdS).

Photoluminiscence of semiconductor clusters provide different energy states available between valence band and conduction band responsible for radiative recombination. The blue band at 450-470 nm was attributed to the donor-acceptor pair transition in which the acceptor is related to the Mn^{2+} vacancy. Such vacancies should be compensated by the predominantly present Na^+ in the zeolite channels or by the formation of $S^-(S^{2+} \text{ hole})$. The negligible red displacement of MnS emission spectrum, at 78K, suggests a strong interaction with the zeolite lattice and a good stability. The higher energy emission peaking at ca 520 nm, observed for CLI-CdS, is consistent with an interaction of Lewis center with cadmium vacancies. The main band at 580 nm observed at 78K for LAU-CdS has been attributed to Cd atoms, products of photochemistry.

The electrical measurements were made as a function of temperature and evidenced an increase in the electrical conductivity and a sharp decrease in the thermal activation energy. The changes in electrical properties arise through systematic transformations in the density of electronic energy levels as a function of the size of the interior, known as quantum size effects.

PHOTOCONDUCTIVITY AND TRANSPORT PROPERTIES OF ARSENIC SELENIDE THIN FILMS

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Amorphous films of the chalcogenide glassy system As_xSe_{100-x} are currently of interest as materials for optoelectronic devices and optical information storage. The composition $As_{50}Se_{50}$ of this system exhibits high light sensitivity in photostructural transformations due to the presence of homopolar As-As bonds.

In the present paper results of a systematic study of steady state and transient photoconductivity characteristics of thermally and laser beam deposited amorphous films (thickness of 1 to 6 μm) of $As_{50}Se_{50}$ are presented. The lux-ampere characteristics of the steady-state photoconductivity are described by the power law dependence. The power index

$0.5 \leq \gamma = \frac{T^*}{T + T^*} \leq 1.0$ is temperature depending with the value of the parameter of localized state

distribution $T^* = 450 K$. The spectral dependence of the photoconductivity for $As_{50}Se_{50}$ amorphous films represents a curve with a broad peak centered at 1.97 eV, and is shifted in high energy region for laser beam deposited films.

The transient photocurrents in amorphous thermally deposited AsSe films were studied in step-function mode of light excitation. The experimental results of the transient photocurrent are interpreted in terms of the multiple-trapping model widely applied to describing charge carrier transport in amorphous semiconductors.

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OPTICAL AND ELECTRICAL PROPERTIES OF AMORPHOUS (GeS_2) $_{100-x}Ga_x$ THIN FILMS

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Results from the study of basic optical and electrical parameters of semiconducting (GeS_2) $_{100-x}Ga_x$ ($x=0, 4, 8, 12$ at.%) amorphous layers have been summarized. The investigation of the optical absorption has shown that the introduction of Ga leads to a shift in the absorption edge towards lower energies in comparison with GeS_2 . The spectral distribution of the refractive index n , accounting the influence of photoexposure, has been specified. The optical energy gap E_g^{opt} has been determined from the Tauc plot $\alpha h\nu = B(E_g^{opt} - h\nu)^2$. The electrical energy gap E_g^{el} has been obtained from the thermal dependence of the conductivity. Both the values of E_g decrease with increasing Ga content. From the current-voltage characteristics, the effective electron mass m^* in the conduction band, the electron work function χ at the Al/Ge-S-Ga interface and the relative dielectric permittivity ϵ have been determined. The experimental data are in agreement with Christov's theory for injected electron currents into dielectric or semiconducting materials. The observed regularities are related to some structural peculiarities in the Ge-S-Ga system studied.

MICROSTRUCTURE OF GLASSES AND GLASS-CRYSTALLINE MATERIALS IN THE SYSTEM $\text{TeO}_2\text{-V}_2\text{O}_5\text{-Ag}_2\text{O-AgI}$

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The ion conducting glasses take important place between the amorphous solid electrolytes. They are perspective materials with promising properties especially when their compositions are based on combination of glass formers, glass modifiers and Ag-oxide or Ag-chalcogenide. The clustering tendency in silver containing materials involves necessity for microstructural studies as obligatory correlation. The appearance of nano- and micro-scale heterogeneities, their interaction with the homogenous glassy matrix and further evolution towards metastable immiscibility formations determine the conducting behavior of the materials.

The subject of this work concerns the structural evolution in glasses and glass-ceramics in the four component system $\text{TeO}_2\text{-V}_2\text{O}_5\text{-Ag}_2\text{O-AgI}$ and the correlation between the microstructure and conductivity of the samples. Our interest towards this system is stimulated by the combination of both non-conventional glass-forming oxides (TeO_2 and V_2O_5) coupled with Ag_2O and AgI .

The precursors used are grade reagent TeO_2 , V_2O_5 , Ag_{20} and AgO . The batches are melted in porcelain crucibles at 600 – 800 °C temperature range and melts were fast cooled between copper plates. Two cross sections containing 50 mol% and 60 mol% AgI were studied for Ag_2O content from 10 to 30 mol%. For comparison compositions without Ag_2O participation (25% AgI , 75% $2\text{TeO}_2\text{-V}_2\text{O}_5$ and 50% AgI , 50% $2\text{TeO}_2\text{-V}_2\text{O}_5$) are also investigated.

The phase formation was studied by X-ray analysis (DRON UM 1, Cu $K\alpha$ -radiation) and the microstructure – by transmission electron microscopy (EM – 400, Philips). Observations were made on small powder particles of the samples and also on replicas from fresh fractured surfaces of the bulk materials. In order to distinguish the initial stage of cluster formation SAED was coupled with BF and DF modes of TEM.

As a basis for data interpretation the already obtained detailed information on the phase diagram of the three component system $\text{Ag}_2\text{O-TeO}_2\text{-V}_2\text{O}_5$ was used. It is established that the sample composition strongly influences phase microstructure. The evolution of the nano- and micro-scale heterogeneities towards liquid phase separation and crystallization is followed. The obtained results are related to the measured conductivity of the materials.

QUANTUM-CHEMICAL MODELING OF THE PARTICIPATION OF HYPERVALENT DEFECTS IN THE RECONSTRUCTION OF THE α -Se STRUCTURE

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The number of hypervalent defects (HD) such as C_4^0 (non-charged atom Se with the coordination number equal 4) and VAP-d (atoms Se_3^+ and Se_1^- at the distance about one bond length) were found in our previous calculations of the structure and defects of α -Se [1-3]. The interaction of these defects with basic structural elements (for example chains) of α -Se network represents a great interest the same as the existence of the defects themselves.

The structure and stability of such defects in α -Se network were investigated in the frame of ab initio B3LYP method with LANL2DZ basis set extended by polarized d-AO with GAUSSIAN-94 package.

The results of calculations show that the closeness in of a Se-Se link of an ordinary chain to the same chain or hypervalent defects (C_4^0 and VAP-d) leads to formation of new hypervalent configurations (with Se coordination number >2). The destruction of these configurations after overcoming of a small potential barrier changes the positions of the hypervalent defects in the α -Se network. The value of the barrier in the case of bond switching with the participation of HD is smaller than for defect-less chain.

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PECULIARITIES OF GAMMA-INDUCED OPTICAL EFFECTS IN TERNARY SYSTEMS OF AMORPHOUS CHALCOGENIDE SEMICONDUCTORS

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The influence of Co^{60} γ -irradiation on the optical properties of amorphous chalcogenide semiconductors of ternary Ge-As-S, Ge-Sb-S, As-Bi-Se, Ge-As-Se, As-Ge-S, As-Sb-S systems was studied.

The radiation treatment of investigated ChVS was performed by γ -quanta in the normal conditions of stationary radiation field, created in the closed cylindrical cavity owing to the concentrically established ^{60}Co ($E=1.25$ MeV) sources. The power of exposure dose was near 20 Gy/sec; the total value of absorbed dose was $(1-5) \cdot 10^6$ Gy. No special measures had been used to prevent the uncontrolled thermal annealing of samples, but the maximum temperature in irradiating camera did not exceed 320-330 K during the whole period of radiation treatment.

The optical measurements were performed using two-beam SPECORD M-40 spectrophotometer ($\lambda = 200-900$ nm). The spectral dependences of the optical transmission coefficient differences (before and after gamma-irradiation) $\Delta\tau(h\nu)$ ($h\nu$ - the photon energy of probing light beam) were chosen as controlled parameters for the investigated effects.

The radiation-induced darkening effect (long-wave or low-energetic shift of the optical transmittance edge described by asymmetric bell-like $\Delta\tau(h\nu)$ curve with strongly pronounced maximum, sharply defined high-energetic and more stretched low-energetic wings) with (or without) changes of optical transmittance was observed for all investigated systems. Static and dynamic components of investigated phenomena were revealed.

Effects in the region of fundamental optical absorption edge were connected with the creations of over- and under-coordinated diamagnetic atomic pairs with opposite electrical charges accompanied by covalent chemical bonds switchings.

Radiation-induced changes in optical transmittance region are associated with macroscopic defects at the level of some coordination spheres (medium range ordering), scattering centers, in homogeneous inclusions, incorporated impurity atoms, thermally produced stressed regions, voids and atomic clusters.

The long wave shift of the fundamental optical absorption edge was observed after radiation treatment. The initial position of this edge restores to some residual value during 2-3 months after γ -irradiation. These results are analysed in terms of the maximum changes in the spectral dependences of the optical transmission differences $\Delta\tau$ before and after γ -irradiation as well as in terms of the integral area S restricted by $\Delta\tau(h\nu)$ curve and photon energy axis. The quantitative expressions for compositional dependence of the total radiation-stimulated effect as well as its dynamic and static components were obtained using the ordered bonds network model.

The regularities of compositional dependencies radiation-induced effects differ in dependence on the degree of stoichiometry. Pseudobinary ternary systems of chalcogenide glasses are characterized by the quasi-linear compositional behavior while non-stoichiometric glasses reveal maximum corresponding to the average coordination number approximately equal to 2.7.

X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES OF THIN $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ CHALCOGENIDE FILMS

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Thin $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ ($x=5, 15, 20, 25$ and 27) chalcogenide films have been investigated by x-ray photoelectron Spectroscopy (XPS). X-ray photoelectron spectra show that there is a peculiarity in the relative intensity ratio of the Sb 4d photoelectron peak associated with Sb_2S_3 to the Sb 4d photoelectron peak associated Sb_2S_5 at an average coordination number Z of $2.65\sim 2.67$. After contamination and photo-oxidation layers were removed from the surface of the films, X-ray photoelectron spectra were measured again. It has been found that, binding energies of the Ge 2p and Sb $3d_{3/2}$ photoelectron peaks, which reflect the electronic structure at lower core energy levels, are independent of Z . However, the binding energies of the Ge 3d and Sb 4d photoelectron peaks are more sensitive to Z and have a discontinuity at $Z = 2.65$.

These peculiarity may indicate the start of a topological phase transition from the layered structure to a three dimensional network at Z of about $2.65\sim 2.67$.

STRUCTURE AND PROPERTIES OF $\text{As}_2\text{Te}_{2.8}\text{Si}_{3.2}$ GLASS

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The As-Te glasses allied with silicon or germanium are interesting because the interaction between very different components results in local chemical environments at variance with those of the crystalline compounds in addition to the topological disorder. This feature strongly influence the physical properties of the glassy materials. The As-Te-Si is important also for the electrical switching, generally possible to occur in Te-based glasses in connection with thermally induced structural transformations.

The ternary glass $\text{As}_2\text{Te}_{2.8}\text{Si}_{3.2}$ has been prepared and studied by differential scanning calorimetry (DSC), X-ray diffraction, density, hardness and electrical transport measurements.

As revealed by DSC analysis, the bulk glass is stable up to 385 °C.

X-ray diffraction measurements have been carried out on a sample at room temperature as well as at two higher temperatures: 365 and 385 °C, below and above the transformation temperature revealed by the DSC. The X-ray data were processed and the atomo-electronic radial distribution functions were computed by a special FORTRAN routine. The results show that the most plausible model for this glass correspond to a continuous random network of atoms bonded according to their covalency requirements. The concentration of homopolar bonds is under the detection limit, when the first peak in the AERDF is analysed.

The density and microhardness of the glass were determined. The electrical conductivity follows an Arrhenius-type curve up to 132 °C. In this region the electrical conductivity exhibits a reversible character. An irreversible change of conductivity occurs above 132 °C. Seebeck coefficient was also measured and the positive type of charge carrier was ascertained.

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THERMALLY-INDUCED STRUCTURAL CHANGES IN COPPER-CONTAINING CHALCOGENIDE THIN FILMS

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Thin-film samples of the system $\text{Cu}_x(\text{AsSe}_{1.4}\text{I}_{0.2})_{1-x}$, $x < 15$ at%, were prepared by the method of thermal evaporation on "cold" substrates in vacuum, using a specially constructed quartz cell as evaporation chamber. The method of transmission electron microscopy was employed to follow the structural changes taking place in the course of thermal treatment of the freshly deposited film samples. It was found that the contents of selenium and copper in the starting glass have a decisive role in determining the structure and properties of the material. The observed microgranular two-phase structures of thin films have a grain size of the order of 10 nm. Heating of the samples to the softening temperature yields the structural transformation in the films from the starting amorphous phase to a new amorphous phase. Also, the temperatures were determined at which partial crystallization takes place, resulting in the separation of crystalline centres of the elemental selenium.

STRUCTURAL-TECHNOLOGICAL MODIFICATION OF As_2S_3 GLASSES

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As_2S_3 glasses structure got in different technological modes was investigated by direct methods of transmission electron microscopy and electronography. As samples we took thin slices with $0.08 - 0.1 \mu\text{m}$ thickness got by cutting of initial massive glasses. All the investigated glasses according to their microstructure were divided into two types: samples got at melt temperature $T = 870 - 1120$ K and melt cooling speed $v = 0.01 - 1.3$ K/s have homogenous microstructure type and glasses got at melt temperature $T > 1200$ K and melt cooling speed $v = 1.5 - 150$ K/s are of heterogenous microstructure type. Different structure models of near and middle order for each type of As_2S_3 glasses got under different technological conditions were investigated.

SCALING FACTOR FOR VIBRATIONAL SPECTRA OF CRYSTALLINE AND GLASSY $\text{As}_2(\text{S,Se})_3$ AND CLUSTERS $\text{As}_n\text{S}(\text{Se})_m$

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In this paper the results of a comparison of frequency positions of Raman lines of amorphous $\text{a-As}_2\text{S}_3$ and As_2Se_3 , crystals $\text{c-As}_2\text{S}_3$ and As_2Se_3 , clusters $\text{cl-As}_2\text{S}(\text{Se})_3$ are given. The Raman line of $\text{a-As}_2\text{Se}_3$ and $\text{a-As}_2\text{S}_3$ are observed at 220 and 340 cm^{-1} , respectively. The relation of these frequencies is 0.64. In the molecular approach the observable vibration lines are related to symmetric vibrations of pyramids $\text{AsS}(\text{Se})_3$ [1]. Under condition of equal force constant, difference in a position of maxima of As_2S_3 and As_2Se_3 is connect with difference of atomic weights of selenium and sulfur and then $\nu_1(\text{As}_2\text{S}_3)/\nu_1(\text{As}_2\text{Se}_3) \sim (m_{\text{Se}}/m_{\text{S}})^{1/2}$. Last relation for $\text{a-As}_2\text{S}(\text{Se})_3$ gives 0.64. In chain approximation the elementary structural unit in As_2S_3 is the chain, constructed from the pyramids $\text{AsS}_{3/2}$ with average length 14.2 Å [2]. The chain, similar on construction, branching in a plane forms a layer in a chain-layered crystal [3]. The relation of frequencies of all most intensive 9 vibration modes in Raman spectra of crystals $\text{AsSe}(\text{S})_3$ gives surprisingly constant rate 0.71 ± 0.02 , the estimations of force constant As-S inside a pyramid give a value $1.26 \times 10^5 \text{ dyn/Å}$ [3]. We carried out the calculations of the vibration spectrum of chain clusters As_2Y_5 ($\text{Y}=\text{S, Se}$), consisting from two pyramids AsY_3 [4]. The values of force constant for As-S bond in clusters are $(2.12\text{-}2.78) \times 10^5 \text{ dyn/Å}$, that is more than was calculated in [3] for crystals. For valence vibrations of non-bridging chalcogen in cluster the values of the scaling factor drop down to 0.66.

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NANOCOMPOSITE CHALCOGENIDES FOR SOLAR ENERGY CONVERSION

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This paper deals with the syntheses, the optical characterization and the study of possible application to energy light conversion using some semiconductors and composites colloidal particles as photosensitizers.

1. Synthesis of CdS colloidal matrix.

We prepared colloidal CDS in Na_2S excess using a method described in the literature. To prevent aggregation we used a stabilizer namely a copolymer styrene/maleic anhydride (1/1). The colloidal solution is yellow, transparent and shows an absorption edge at about 550 nm. Particle size was determinate both from absorption and emission spectra and we obtained $d_p \sim 70 \text{ \AA}$, a Q particle domain. The CDS sol prepared by us is polydisperse and the determinated average particle diameter characterised the most particle number.

We optimized this model system for hydrogen generation from water using prepared CDS as photosensitizer.

2. Synthesis of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ colloidal particles.

One coprecipitated CdS and ZnS in Na_2S excess too, and obtain a composite with the formula $\text{Cd}_{0.53}\text{Zn}_{0.47}\text{S}$. The addition of Zn assure a more negative potential of the composite than that of pure cadmium sulphate, what favored the reduction of water to generate H_2 .

3. Synthesis of $\text{Cd}_{1-x}\text{Cu}_x\text{S}$ colloidal particles.

One coprecipitated CdS and CuS in Na_2S excess too, and obtain composites with different amount of Cu. In our experimental conditions, the addition of Cu did not modify the activity of pure cadmium sulphate particle, and did not favored the reduction of water to generate H_2 .

4. Synthesis of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ semimagnetic colloidal particles.

Synthesis of $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ and $\text{Zn}_{1-y}\text{Mn}_y\text{S}$ nanoparticles with different x and y value was performed in microheterogeneous medium. We used as stabilizer agent polyacrylic acid and hexamethyl polyphosphate and obtain $\text{Cd}_{0.5}\text{Mn}_{0.5}\text{S}$ and $\text{Zn}_{0.54}\text{Mn}_{0.46}\text{S}$. Size particle and composition are controlled independently using the absorption spectra which show, at fixed composition, a quantum size effect. We observed, also, that the energy gap value decreases when manganese ions are inserted in to the matrix, and this will increase the efficiency of water reduction to generate H_2 .

STRUCTURAL INTERPRETATION OF PHOTOINDUCED IRREVERSIBLE CHANGES IN $\text{Ga}_{10}\text{Ge}_{25}\text{S}_{65}$ CHALCOGENIDE GLASSES

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The present work shows the photoexpansion effect observed in $\text{Ga}_{10}\text{Ge}_{25}\text{S}_{65}$ glasses when exposed to above band gap light (3.52 eV). A volume change of about 5% is reached in bulk samples by controlling time exposure and power density. In order to evaluate the photostructural change infrared and Raman spectra for bulk $\text{Ga}_{10}\text{Ge}_{25}\text{S}_{65}$ glasses have been measured before and after exposure. The observed changes in the region of stretch vibration of the chalcogenide atoms is direct evidence for the occurrence of large structural changes in local bonding configuration caused by optical irradiation. It have been shown that under the laser irradiation the data support a generalized chain-crossing model rather than a random-covalent network model showing that the bonding tendency of the chalcogenide atoms is to form rings rather than chains.

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CHALCOGENIDE FIBRE DISPLACEMENT SENSOR

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Fibre optic technology offers the possibility for developing of a variety of physical sensors for a wide range of physical parameters. The main advantage of fiber optic sensors lies in their dielectric construction, providing electrical isolation, immunity from electromagnetic fields, small dimensions, and compatibility with optical fibre technology. A large number of fiber sensors in production are based on intensity modulation of the light either outside the fiber or within it. In the case of intensity sensors the physical perturbation to be measured interacts with the fibre or some device attached to the fibre to modulate the intensity of the light as it travels through the fiber. Intensity modulated fiber sensors have been demonstrated to be efficient for different applications. A variation of internal-modulation sensors are the microbending-loss sensors, which are characterized by a relatively simple construction, good performances and compatibility with multimode fibre technology.

A very effective configuration for the microbending-loss sensors is that based on clad mode detection. For clad modes detection the end segment of the fiber is bent and placed in an integrating sphere.

The use of chalcogenide rather quartz fibre optic highly increases the sensitivity of the sensor. Experimental set-up, transmission characteristics and technical parameters are presented.

ANALYSIS OF THE Z-SCAN MEASUREMENT TECHNIQUE OF THE OPTICAL NONLINEAR PROPERTIES

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Extension of the state of the art in all-optical and opto-electronic based systems for future applications will rely on the development of new or refined existing optical materials. Chalcogenide glasses are the main candidates for such applications because they exhibit extremely low loss for light transmission in a large spectral range and have strong glass forming tendencies similar to that of traditional oxide glasses. The stability of such materials is largely dependent on the intrinsic absorption of the material. Additional nonlinear effects can develop with the increasing of the irradiation power. There are a lot of methods for nonlinear optical properties diagnosis, but that known as "Z-scan" seems to be the simplest and most popular technique. In this method, the sample is translated in the Z-direction along the axis of a focussed Gaussian beam, and the far field intensity is measured as function of sample position. Analysis of the intensity versus sample position (the Z-scan curve), gives nonlinear absorption in the third order susceptibility.

Starting from 1990, both theoretical and experimental fundamentals of the method were published in numerous papers, which tried to refine and to improve this powerful tool applicable to a large variety of optically interesting materials.

In this paper we will analyze how can be minimized various limitations of the method originated in:

- non-uniformity of the intensity distribution and fluctuations of the laser beam (intensity, pointing stability);
- the etalon effect, especially for samples with large refractive index ;
- the presence of an optical anisotropy;
- the coexistence of many nonlinear mechanisms, with different relaxation time.

It will be shown various different versions of the method developed according to requirements imposed by sample geometry and structure. There will be revealed how the sensitivity of the method can be improved by an appropriate choice of the aperture. A comparison between the Z-scan standard version and EZ-scan version is the proof. Solutions regarding how to separate different contributions to the nonlinear response will be also discussed. Experimental results in good agreement with those obtained with other more sophisticated methods, like four wave mixing, for a large variety of materials and sample configurations, is the reason for which the Z-scan technique became so popular.

PROGRAMMABLE METALLIZATION CELL MEMORY DEVICES BASED ON AMORPHOUS CHALCOGENIDES

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Metals such as silver or copper can be photo-dissolved in chalcogenide glasses, e.g., arsenic sulfide or germanium selenide, to form solid solutions. Even with metal concentrations as high as tens of atomic percent, these ternaries have resistivities that are many orders of magnitude higher than thin films of the pure metal. If electrodes are formed in contact with a layer of the solid solution, an anode, which has oxidizable Ag or Cu and an inert cathode, and a voltage is applied between them, the positively charged metal ions will migrate toward the cathode region. At small applied bias (a few hundred mV) in structures which are commensurate with state-of-the-art integrated device geometries, the ions will come out of solution at the cathode to form a stable metallic electrodeposit which may be made to extend from the cathode to the anode in considerably less than 1 μsec . The low resistance metal electrodeposit acts to short-out the relatively high resistance glass and hence the overall resistance of the structure can be reduced by many orders of magnitude via this non-volatile electrically-stimulated deposition process (see Fig. 1). A reverse bias will cause electrodisolution of the metal link, returning the device to a high resistance state and this write-erase cycle may be repeated tens of millions of times. This reversible switching effect is the basis of the Programmable Metallization Cell (PMC) memory technology.

The key attributes of a high density solid state memory are (1) low internal voltage to allow the close packing of structures without breakdown and crosstalk and to reduce power supply requirements, (2) extremely low power/energy consumption to avoid problems with power density and heating in closely-packed structures and to facilitate the use of small battery power sources, and (3) the ability for the devices to be scaled to minimum lithographic dimensions. PMC memory meets these requirements. For example, the sub-half volt operation (which lies beyond the current end of the International Technology Roadmap for Semiconductors), combined with low programming current and time means that the energy required to reduce the resistance of the device by several orders of magnitude is significantly less than 1 pJ per cell, thereby meeting conditions 1 and 2 above. The "active-in-via" (AIV) variant of the PMC technology has the solid solution wholly contained within a via hole in an inter-metal dielectric layer (see Fig. 2). This is an extremely compact structure and lends itself well to scaling. Indeed, we have been able to demonstrate the operation of AIV devices as small as 50 nm in diameter and believe that more aggressive scaling is possible and so condition 3 is also met. PMC also adds the possibility of increased data density through multi-bit storage and layering of the storage structures above the silicon circuitry.

OPTICAL AND ELECTRICAL PROPERTIES OF AS-DEPOSITED LPCVD SiO_xN_y THIN FILMS

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The silicon oxynitride (SiO_xN_y) films have several applications in opto- and micro-electronics technology: thin gate dielectrics, optical wave guides and membranes for microelectromechanical systems (MEMS). In some applications it is necessary a controllable variable refractive index of the silicon oxynitride films. In others, the defect density at the Si/ a- SiO_xN_y interface should be well controlled. This paper deals with these issues and an investigation of the relationship between deposition parameters and the physical properties of the a- SiO_xN_y films is done.

Amorphous silicon oxynitride films of various compositions were deposited by low-pressure chemical vapor deposition (LPCVD) at temperature around 800°C and 400 mTorr, using mixture of $\text{SiCl}_2\text{H}_2\text{-NH}_3\text{-N}_2\text{O}$. The investigations on optical and electrical properties of the samples were made using spectroellipsometry and capacitance-voltage measurements. Optical and microstructural parameters of the films were calculated from spectroellipsometry data using different approaches (Bruggeman-EMA, Cauchy, Sellmeier and Wemple-Di Domenico). The refractive index dispersion curves were well fitted with both the Cauchy and the Sellmeier theoretical models. The equivalence between the parameters that characterize the two models is established. As the Wemple and Di Domenico approximation applied to our samples has shown, the optical band gap values decrease with the increase of the nitrogen content in the SiO_xN_y films.

The analyses of 1 MHz capacitance-voltage characteristics revealed low densities of the interface traps. This is attributed to the nitrogen incorporation at the $\text{SiO}_x\text{N}_y/\text{Si}$ interface, which leads to suppression of interface trap generation.

GLASSY TRANSFORMATION AND STRUCTURAL CHANGE IN $\text{Ge}_2\text{Sb}_2\text{Te}_5$ STUDIED BY IMPEDANCE MEASUREMENTS

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The transition from amorphous-to-crystalline (fcc) has been investigated in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin film alloys. This composition is the most frequently used for erasable optical memory devices. The phase transition was monitored using *in situ* impedance measurements as a function of temperature. The results were analyzed using the Maxwell-Wagner and brick models. From the impedance measurements it is possible to detect the appearance of nucleation centers in samples heated at temperatures below crystallization. In samples treated at temperatures above crystallization, the increase in the volume fraction of crystalline material due to the increase in the temperature is also deduced from the impedance measurements.

From our investigation we have shown that impedance measurements are a sensitive method to analyze the crystallization process in chalcogenide materials.

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PHOTOSENSITIVITY IN ANTIMONY BASED GLASSES

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Several studies have been reported on the photosensitivity of amorphous materials based on chalcogenides. The photoinduced phenomenon is generally observed by a change of the physical or chemical properties under irradiation to light having a photon energy comparable to the bandgap. Besides that, antimony oxide glasses present higher thermal stability against devitrification and higher refractive index. In the present work, we will present new glass forming systems based on Sb_2O_3 - SbPO_4 , Sb_2O_3 - SbPO_4 - WO_3 . The thermal and optical properties of these glasses will be presented. Extended x-ray absorption fine structure were performed at LURE facility in Orsay France to obtain structural information and determine coordination number of Sb.

Glass compositions explored in the system Sb_2O_3 - SbPO_4 have been exposed to UV laser (Argon, $\lambda = 350 \text{ nm}$, $P = 250 \text{ mW}$). A change on the coloration of the irradiated area is observed after 30 min of irradiation. The observed phenomenon is evaluated by XANES measurement. The XANES spectra, studied for the L_3 edge, show an increase of the coordination number for Sb atoms induced by exposure to light. XANES spectra, for the L_1 edge, suggest a change in the oxidation state of Sb atoms. This process is reversible, one time glass samples is heated at T_g , glass transition temperature.

ELECTRODEPOSITION OF Bi_2Te_3 , Sb_2Te_3 AND $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ FROM ORGANIC MEDIA

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There are presented the conditions for codeposition of stoichiometric chalcogenides as *n* and *p* layers of Bi_2Te_3 and Sb_2Te_3 that are thermoelectric materials. The electrodeposition in organic media like ethylene glycol takes place according to Faraday's law to a current efficiency close to 100%. The organic deposition solutions with appropriate concentrations of elemental species of Bi, Sb, Te were used in order to reproduce in electrodeposited layers the chalcogenides like Bi_2Te_3 and Sb_2Te_3 as well as ternary *n* and *p* $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ electrodeposited compound.

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OPTICAL PROPERTIES OF THE GLASSY THIN FILMS FROM Ge - Se - Ga SYSTEM

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A study of the optical spectra of amorphous $(\text{GeSe}_4)_{1-x}\text{Ga}_x$ and $(\text{GeSe}_5)_{1-x}\text{Ga}_x$ chalcogenides in spectral range 460nm - 1400 nm is performed.. Samples used were in a bulk and thin film form. Bulk glasses are prepared by monotemperature synthesis from elements with 4N purity in evacuated quartz ampoules. Thin films were deposited by vacuum evaporation at a residual pressure 10^{-3} Torr using optical glass as film substrate. For the measurements the samples were placed in the cryostat and kept in vacuum. A 75 W halogen lamp with monochromatic light was used to illuminate the sample. The intensity of incident and transmitted light through the sample was measured with silicon detector at the lower and germanium detector at the longer wavelength.

From the absorption spectra optical energy gap (E_g^4) was determined. The optical-absorption edge is described using the non-direct transition model proposed by Tauc and the optical band gap - E_g^T is calculated from the absorption coefficient values by Tauc's procedure. Optical absorption was described in medium-absorption region, according to Urbach's rule and the slope of the Urbach's tail was calculated.

The compositional dependence of the band gap was discussed. A relation between average coordination number, composition and optical characteristics was obtained. From the transmission spectra, the optical constants were calculated using an optical-characterization method based on creating the upper and the lower envelope curves of the spectrum. The dispersion of refractive index (*n*) and absorption coefficient (*k*). The values of refractive index and absorption coefficient are considered as a function of average coordination number (*z*) of covalent bonds per atom.

The observed regularities are related to some structural peculiarities in the ternary systems investigated.

CHEMICALLY PREPARED NANOCRYSTALLINE PBS THIN FILMS

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PbS nanocrystalline thin films were prepared by Chemical Bath Deposition (CBD) technique. The deposition bath was doped with Bi^{3+} ions. A comparative study between “standard” and nanocrystalline PbS thin films was performed. We denoted “standard” the film obtained after 1 hour and “nanocrystalline” the films obtained after 17 minutes as deposition time. The other deposition parameters (bath composition, pH, temperature) were kept constant for the all depositions. The morphological properties of the films were determined by SEM analysis. Also, the electrical and photoelectrical behaviour were investigated for the both type of PbS films. The nanocrystalline film had a very high electrical resistance ($10^{10} \Omega/\square$) compared with the “standard” film (10^5 - $10^6 \Omega/\square$). Both types of films proved to be sensitive to the surrounding atmosphere, air or vacuum. It was observed continuous increase of photosensitivity with the temperature decreasing in case of nanocrystalline film. In case of “standard” film the photosensitivity has a maximum at about -80°C . Thermally Stimulated Current (TSC) measurement had shown the presence of an important trap concentration in case of nanocrystalline film, probably due to the large amount of disordered regions.

COMPOSITIONAL TRENDS OF THE PROPERTIES IN Ge-Se-Ga CHALCOGENIDE GLASSES

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Chalcogenide glasses have been attracted great attention as promising materials for different applications. Due to some unique optical and electrical phenomena, they are expected to be promising material in the IR optics, microelectronics, etc. Bulk glasses of $(\text{GeSe}_4)_{1-x}\text{Ga}_x$ and $(\text{GeSe}_5)_{1-x}\text{Ga}_x$ systems, with 5, 10, 15, 20 at % Ga were prepared with melt-quenched technique, using 4N purity elements of Se, Ge and Ga.

The density was measured hydrostatically in a medium of diiodine-methane. The molar volume and the compactness were calculated. The values of the density increase regularly with the addition of Ga to the Ge-Se matrix. The increasing in Ga content leads to a structure change due to a gradually replacement of Se atoms by Ga atoms. The bond energy of Ga-Se bonds is higher than Se-Se bond energy. The density of the Ga atoms is bigger than the density of the Se, as result the density of the system increases too.

The strength of the chemical bond is connected to the "free volume" in material or density of the defects in the sample. The biggest changes in the structure (higher sensitivity) are expected in the samples with small compactness of the structure.

The number of constraints per atom (N_{co}) as a function of the average coordination number is calculated. It is seen that the number of degrees of freedom increases with gallium addition and the flexibility of the system increases as a consequence.

These glasses are assumed to be composed of cross-linked structural units of tetrahedral GeSe_2 and pyramidal Ga_2Se_3 and excess, if any of Se. An extremum in properties could expect at the respective tie-line compositions of the two systems where only presence of GeSe_2 and Ga_2Se_3 units are presented with any Se in excess. Bonds are formed in the sequence of decreasing bond energies until all available valences for the atoms are saturated. After all these bonds are formed, there are still unsatisfied Se valences, 'excess bonds', which must be satisfied by the formation of Se-Se bonds. The quantity of Se-Se bonds is bigger in the system GeSe_5Ga , which results in an increase of the compactness. The compactness in the GeSe_4Ga glasses varies in narrow limits.

RAMAN-NATH DIFFRACTION IN THIN As_2S_3 GRATINGS

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The investigation of the light diffraction on the holographic gratings induced in amorphous chalcogenides is important for a better understanding of the various photo-induced effects that occur in these materials and also for their applications in holography, optical imaging and optical information processing [1].

We have experimentally studied the diffraction on phase gratings induced in thin amorphous As_2S_3 films, in the Raman-Nath regime. In this diffraction regime ("thin" gratings), the restrictions imposed by the Bragg diffraction condition are not present, and many diffraction orders can appear in the diffraction spectrum of the reading beam. The number and intensity of the diffraction orders depend on the grating phase modulation index (related to the non-linearity of the process).

The gratings have been induced using an Ar laser (514.5 nm wavelength). At this incident wavelength, the absorption coefficient and the refractive index are both modulated and a complex, amplitude and phase grating, is recorded in the As_2S_3 film. In order to discriminate between the contribution to diffraction produced by the amplitude and the phase gratings, a He-Ne laser beam has been used for probing. In this case, the complex grating acts almost as a pure phase grating. We have studied the dynamics of the phase grating, by monitoring the temporal evolution of the various diffraction orders intensities produced by the He-Ne reading beam.

The diffraction spectra have been analyzed in the frame of Raman-Nath diffraction theory, which gives a correct description of the diffraction for small phase modulations. For high modulations of the phase grating, the Bessel function approximation used in the Raman-Nath model is not sufficient for a correct prediction of the diffraction orders intensities, and a more accurate theory of the diffraction is necessary to be considered [2].

The results of our study indicate a strong variation of the refractive properties of the As_2S_3 and a high modulation of the laser induced phase grating. According to the Ref. [3], where no relief structure caused by the incident interference pattern (514.5 nm) was reported, we suppose that the phase grating is produced by the modulation of the refractive index of As_2S_3 . This could be due to the stress distribution inside the thin film, a consequence of the photo-structural changes produced by the incident fringe pattern, which is connected to the refractive index modulation through the elasto-optic effect [4]. Further experiments are needed to verify these hypotheses.

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PHOTOINDUCED PHENOMENA IN TUNGSTATE FLUOROPHOSPHATE GLASSES

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Photosensitive glasses have attracted considerable interest regarding to their potential ability to be used in optical switching or memories devices [1]. This photosensitivity was first observed in 1978 in germanosilicate glasses as a change of the refractive index value under laser illumination [2] and a lot of studies were performed to try to explain the origin of this phenomenon [3-7]. Also several works have been reported on chalcogenide materials [8] and recently on fluoride glasses [9].

In this work, we will present for the first time a study of photoinduced phenomena observed on new tungstate fluorophosphate glasses based on the $\text{NaPO}_3\text{-BaF}_2\text{-WO}_3$ ternary composition. The phase diagram was determined and the evolution of the physical and optical properties was studied regarding to the tungsten oxide concentration. The evolution of these properties were compared with the evolution of structural units around the tungsten oxide. Compositions with large amount of WO_3 (>35%) have been exposed to UV irradiation at 350 nm. during 60 min using 400 mW power density. Photodarkening and change on the glass surface are observed and characterized by AFM and scanning electronic microscopy. Structural study also will be reported based on Raman data.

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ON THE ELECTRICAL AND OPTICAL PROPERTIES OF POLYCRYSTALLINE ZnSe FILMS DEPOSITED BY THE QUASI-CLOSED VOLUME TECHNIQUE

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Zinc selenide (ZnSe) is one of the most promising materials for modern technology of solid-state devices (electro-luminescent devices, ultrasonic transducers, lasers, photodetectors, etc.). A great number of these devices are at present made by using thin films.

In paper some electrical and optical properties of polycrystalline ZnSe films are studied.

The films ($d=0.23-1.50\ \mu\text{m}$) were deposited by the quasi-closed volume technique under vacuum onto glass substrates. The film structure was studied by the X-ray diffraction technique and scanning electron microscopy (SEM).

In order to obtain samples with stable structure and reproducible properties, all films, after deposition, were subjected to the heat treatments, consisting of 3-5 heating/cooling cycles within a temperature range $\Delta T=300-570\ \text{K}$. The study on the electrical conductivity provided valuable information regarding the structure modifications occurring during these heat treatments.

SEM studies showed that films have a polycrystalline structure.

For heat-treated samples, the values of activation energy of electrical conduction, calculated from the $\ln \sigma=f(10^3/T)$ curves in the intrinsic domain, ranged between 2.50 and 2.70 eV. These values are in good agreement with those reported for bulk samples of this material.

The experiments showed that absorption spectra are strongly influenced by the preparation conditions of films. The values of energy gap, calculated from the absorption spectra ranged between 2.60 and 2.80 eV.

The nature of the mechanism of electrical conduction is studied samples is also discussed.

MICROPARACRYSTALLINE MODEL FOR THE STRUCTURE OF NON-CRYSTALLINE CHALCOGENIDES

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There is a continuous interest in the medium range order (MRO) of non-crystalline chalcogenides. The most remarkable manifestation of MRO is the so-called "first sharp diffraction peak" (FSDP) or "pre-peak" in the structure factor, $S(Q)$.

The attempts to interpret various experimental observations have led to several models of MRO.

In this paper the MRO was analyzed in the frame of the paracrystalline theory. The theory, earlier applied to lamellar and fibrous structures, finds in the chalcogenide glasses an interesting working case.

In the frame of a microparacrystalline model, the characteristics and the complex behaviour of the FSDP are satisfactorily explained. From a typical Hosemann plot it is possible to define a new parameter for the characterization of glasses: the paracrystalline distortion, g .

We have calculated both the mean paracrystal thickness and the paracrystalline distortion for various amorphous and glassy chalcogenides and other covalent amorphous materials as e.g. arsenic or SiO_2 .

The results are rewarding and they have shown that the calculated parameter starting from the X-ray diffraction pattern, can be used in the characterization at a fine scale of the differences between various chalcogenide samples, including those subjected to various annealing treatments, to pressure, to mechanical stress, to light or other radiations, etc...

The new microparacrystalline model seems to be of interest for understanding the crystallization and melting processes in chalcogenides and, more generally, in the large class of covalent glasses.

ON THE STRUCTURAL CHANGES ACCOMPANYING THE PHOTOVITRIFICATION PHENOMENON IN $\text{As}_{50}\text{Se}_{50}$ THIN LAYERS

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Amorphous chalcogenides exhibit a wide variety of photoinduced structural transformations. A flexible structure due to the presence of lone-pair electrons, on the one hand, and localization of carriers because of the disorder, on the other hand, are responsible for this light-induced structure-related metastability.

Let us consider a process for producing amorphous state, namely the athermal light-induced vitrification of $\text{As}_{50}\text{Se}_{50}$ thin layers. This phenomenon has been characterized structurally, by means of X-ray diffraction measurements, far-infrared and differential infrared spectroscopies, and optically by use of two different methods, enabling the determination of the average thickness and refractive index of a wedge-shaped thin layer. We will focus our attention on the structural changes, which accompany the photovitrification phenomenon of $\text{As}_{50}\text{Se}_{50}$ layers. It is important to note that the photoinduced changes observed in the optical properties of $\text{As}_{50}\text{Se}_{50}$ layers are much more pronounced than those in stoichiometric layers.

The optical study shows that illumination of the chalcogenide samples produces a reversible photodarkening effect. In well-annealed As-rich chalcogenide samples, As – As bonds play a significant role in reversible photodarkening. As a consequence of illumination, an increase in the As – As bond concentration leads to a decrease of the Tauc gap, owing to formation of electronic states associated with such bonds, at the top of the valence band. Similarly, the subsequent annealing of the sample will lead to a decrease in the As – As bond concentration, and therefore, to an increase of the Tauc gap, because breaking of As – As bonds will replace electronic states in the gap associated with these homopolar bonds, by non-bonding As states located near the conduction band edge.

On the other hand, the decrease in the average thickness of the layers, due to annealing, is a clear sign of a thermal densification process, whereas the increase, which takes place with illumination, constitutes a photoinduced volume expansion. A correlation between the changes in thickness and optical bandgap for illumination, as well as for post-illumination annealing and post-annealing illumination, has been established. The observed changes in thickness and optical bandgap in $\text{As}_{50}\text{Se}_{50}$ layers are explained on the basis of the 'repulsion and slip' model.

EFFECT OF OBLIQUE DEPOSITION ON OPTICAL AND ELECTRICAL PROPERTIES OF As_2S_3 AND As_2Se_3

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During past four decades devices based on amorphous and disordered materials have grown in importance. Their significant impact has been on two of the largest and most fundamental areas of our global economy – information and energy. The atomic bond in these materials is covalent, while it can be modified as metallic and ionic. It is this flexibility which provides a variety of properties and applications. The ability of amorphous materials to be engineered at molecular level and fabricated by vapour deposition process in highly uniform, large area structures has permitted them to be used in wide range of devices for sensing, encoding, switching, transmission and storage of information. It has also enabled the development of new pollution free technology for generation of electrical energy.

In this paper, the effect of oblique deposition on optical and electrical properties of As_2S_3 and As_2Se_3 thin films has been studied. The samples were deposited at an angle of 80° , this being the angle between the normal to the substrate and the direction of incidence of the evaporated atoms. At this deposition angle, the density of atoms is found to be minimum and changes in the properties are expected to be maximum. The films were deposited by vacuum evaporation technique on to a glass substrate at room temperature in a vacuum of approximately 1×10^{-6} torr. X-ray diffraction results show that the films were amorphous in nature. The band gap was found to be independent of the angle of deposition. The refractive index and absorption coefficient have been obtained using transmission spectra. Variation of refractive index and extinction coefficient with wavelength has also been investigated.

THE STABILITY OF CADMIUM CHALCOGENIDE PIGMENTS IN THE PROCESS OF LASER CLEANING OF PAINTED SURFACES

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Pigments based on cadmium selenide sulfides and cadmium sulfide were analysed as regarding their structure and stability against laser irradiation, a new technique for cleaning the painting surface in artwork restoration. X-ray diffraction and scanning electron microscopy (SEM) were used to this purpose. The pulsed Nd:YAG laser radiation determines the release of some sulfur from the red pigment $\text{Cd}(\text{S}, \text{Se})$ and significant decrease of the average size of the crystallites. The colour turns to dark red. For yellow pigment (CdS) no change of crystallite size was detected after laser irradiation, but small changes of lattice parameters of crystallites account for a tendency to darkening.

ELECTRON BEAM INDUCED PATTERNS IN GeS₄

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The results of a systematic study of pattern formation by an electron beam in GeS₄ are reported. The effect of the type of substrate on the final form of the patterns has been investigated. In addition, the dissolution of silver into the chalcogenide matrix assisted by electron irradiation has been studied. This effect has potential applications in electron beam lithography. The effects observed in this study support the electrostatic model proposed by Tanaka [1] for pattern formation in these materials.

In order to elucidate whether the conductivity of the substrate is important for pattern formation an experiment has been designed in which two identical samples were grown on different substrates and subsequently irradiated keeping all the parameters the same. The substrates were pure silicon and 0.5 μm of silica over pure silicon. After irradiation the patterns were measured with an atomic force microscope (AFM). Patterns of more than 500 nm height were formed on the sample grown on silica, while in the sample grown on silicon the patterns did not exceed 30 nm.

The formation of patterns in samples grown on the silicon substrates coated with a thin film of silver did not show a significant dependence on the electron beam set up. Electron beam irradiation induced the dissolution of silver into the chalcogenide only in the interaction volume, while the remainder of the sample was unaffected. It was then straightforward to remove the remaining GeS₄ and silver by etching with NaOH and HNO₃. It is believed that the formation of these patterns is induced by the expansion of the material in the irradiated area due to doping with silver, rather than by a continuous migration of silver towards the irradiated area.

THERMOSTIMULATED RELAXATION OF SbSI GLASS STRUCTURE

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In this report we submit results of the investigations of vibrational spectra and dielectric properties (ϵ and $\text{tg}\delta$) of glassy SbSI, which in crystalline state has distinctly defined ferroelectric properties.

Glassy SbSI was obtained under swift cooling of the melt – 200 K/s. Characteristic temperatures of thermal effects for glass SbSI are defined: glass-forming temperature $T_g = 350$ K, crystallization temperature $T_c = 370$ K, melting temperature $T_m = 670$ K.

IR and Raman spectra investigations were conducted under $T = 300$ K in frequency range $400\text{--}50\text{ cm}^{-1}$. Dielectric properties were investigated in temperature interval $200\text{--}510$ K in frequency range $10^2\text{--}10^5$ Hz.

Investigations showed that under repetition of heating-cooling cycles in temperature range from room to glass-forming T_g , dependence character $\epsilon(T)$ and $\text{tg}\delta(T)$ in SbSI glass practically does not change. ϵ and $\text{tg}\delta$ weakly depend on T . The further increase of temperature leads to irreversible processes evoked by structural relaxation from non-equilibrium state of the glass to the crystalline state. Crystallization of SbSI glass is accompanied by the sharp growth of ϵ and anomaly on $\text{tg}\delta(T)$ dependence. At $10^3\text{--}10^4$ Hz frequencies in $300\text{--}350$ K temperature range we notice a shoulder that is connected with glass structure relaxation and its transition into the polar state. We have investigated thermocycling influence on dielectric parameters of crystallized SbSI glasses. It is proved that annealing temperature growth leads to crystalline grains growth and to anomalies ϵ and $\text{tg}\delta$ amplification. In crystallized samples we notice strongly smeared ferroelectric phase transition.

The given conclusions are confirmed by the results of investigations of vibrational spectra, IR spectrum of SbSI glass contains absorption bands at 290 and 165 cm^{-1} that correspond to vibrations of $\text{SbS}_{3/2}$ and SbI_3 structural groups. These structural units form glass matrix. Analogous result is obtained after Raman spectra investigation. Besides the bands at 290 and 165 cm^{-1} we defined weak bands explained by presence in glass structure structural groups with homopolar bonds Sb–Sb and S–S. These results prove „quasieutectic” model of SbSI glass. IR spectrum of crystallized glass is similar to IR spectrum of SbSI crystal. With the increase of annealing temperature, the spectrum constantly changes to the spectrum of the crystalline state.

ON THE ELECTRICAL AND OPTICAL PROPERTIES OF THE STRATIFIED TELLURIUM THIN FILMS

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The investigations relating to the electrical and optical properties of Te thin films indicate that these strongly depend on the preparation conditions and film thickness.

Our X-ray diffractometric studies showed that Te thin films prepared by thermal evaporation in vacuum are characterized by a stratified structure. For relative smaller thicknesses ($0.10\text{--}0.20\mu\text{m}$) the film microcrystallites have a preferred orientation with their c-axis parallel to the substrate. As the film thickness increases, this orientation is modified and c-axis of microcrystallites becomes obliquely oriented to the substrate. The thicknesses of these sublayers depend on the deposition conditions.

Varying these conditions, films with about identical total thicknesses but having different thicknesses for the two sublayers may be obtained. In present paper, the effect of this specific stratified structure, on the some electrical (conductivity, hole mobility) and optical (absorption coefficient, refractive index) properties of the Te thin films has been investigated.

The investigated samples have been deposited by thermal evaporation in vacuum of Te powder onto glass substrates. The substrate temperature was kept constant during the film growth and its value varied from 290 to 450K. The film thickness ranged from 0.70 to 1.40 μm , deposition rate varied between 2 and 25 nm/s and incidence angle of the Te vapours on the substrates was within the range $0^\circ\text{--}60^\circ$.

The experimental results revealed an important dependence of respective properties on the film thickness and preparation conditions. As, for the textured films, the electrical conductivity, optical absorption and refractive index have greater values in comparison with those for films with preponderantly obliquely oriented crystallites. We concluded that for a correct interpretation of the thickness dependence of physical properties of Te thin films it must take into account the modification of the film microstructure during their growth, in addition to other factors.

The obtained results are discussed in correlation with both the specific character of chemical bonds in the crystal and with their anisotropic properties.

EXTENDED X-RAY ABSORPTION FINE STRUCTURE STUDY ON Bi MODIFIED GeS BULK GLASSES

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EXAFS measurements have been performed from the Ge K edge and Bi L_{III} edge on GeS₂Bi glasses with 8 and 16 Bi at. %, and on crystalline Bi₂S₃. As expected, Ge is found to be four-fold coordinated with S atoms. It is also found that Bi is only coordinated with S with a coordination number CN= 4. This result for the CN of Bi contradicts the conclusion of Elliot and Steel [1]. On the basis of the obtained CN of Bi, it is possible to exclude the presence of Bi₂S₃ microcrystalline inclusions and to assert that these glasses are homogeneous at the microscopic level.

HOLOGRAPHIC RECORDING IN NANO-SIZED As₂S₃ FILMS

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The diffraction gratings in 10, 15 and 20 nm thick As₂S₃ films are recorded using a totally reflected reference wave. The recording is achieved by the interference between this surface propagating in homogeneous (evanescent) wave and homogeneous wave. The diffraction efficiency dependence on the exposure is investigated. The maximum measured values are 0.0005%, 0.004% and 0.007% for 10, 15 and 20 nm thick films, respectively. Despite of the relatively low efficiency, we succeed in the focal plane quasi- Fourier USAF test target hologram recording. A random-phase mask in the object plane is used in order to diminishes the influence of the recording medium limited dynamic range.

EVANESCENT-WAVE RECORDING IN NANO-SIZED LAYERS

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The theoretical background of an optical holographic recording in very thin films is given. The interference fringes are stored by surface propagating evanescent waves. Such waves are created by the total internal light reflection (TIR).

The experimental verification of the theory is made. The holographic grating with 454 nm period has been recorded in 29, 39 and 74 nm thick As_2S_3 films. The diffraction efficiency dependence on the exposure time is investigated. The polarization behavior of TIR surface holograms is similar to that of the thick Bragg holographic gratings. The possible applications of this holographic recording are also discussed.

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OXYGEN EFFECT ON THE OPTICAL PROPERTIES OF CHALCOGENIDE GLASSES

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Chalcogenide glasses are known to be good hosts for Ho^{3+} lasers and, in fact, efficient emission was observed at around 2 μm mainly due to low phonon energies observed in these systems. Moreover lanthanide ions are easily dissolved in these glasses and large pieces can be prepared without major difficulty. However the absolute control of stoichiometry and elimination of impurities are difficult tasks to be considered together since sealed ampoules are used in the preparation experimental routine. In the system $\text{Ga}_2\text{S}_3\text{-La}_2\text{S}_3$ glasses may be obtained in a narrow range of compositions. This range can be enlarged if oxides are added. Oxide containing sulfide glasses are in fact more stable against crystallization than the pure sulfide ones. However optical properties should be poorer. In this work we present some results considering this compromise among stoichiometry, stability against crystallization and optical properties for glasses in with compositions (mol%) $x\text{Ga}_2\text{S}_3(70-x)\text{Ga}_2\text{O}_3\text{-}30\text{La}_2\text{S}_3$ with $x=0\text{-}70$. Glasses were prepared in a open set-up which allows easy elimination of impurities and control of stoichiometry. Spectroscopic properties of Ho^{3+} containing glasses were evaluated in this sense. Judd-Ofelt intensity parameters and emission at 2 μm were discussed and related to glass compositions.

STRUCTURE AND PROPERTIES OF CHALCOGENIDE GLASSES IN THE SISTEM $(\text{As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$

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Several glassy samples in the pseudo-binary system $(\text{As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$ ($x=0; 0.05; 0.25; 0.45; 0.65$) have been investigated by X-ray diffraction. The atomo-electronic radial distribution functions (AERDF) were calculated by Fourier transforming the X-ray diffraction data collected from powdered samples obtained by crushing as-cast glassy ingots.

Careful analysis of the AERDF curves has shown that a good model for the structure of these glasses seems to be that with mixed disordered $(\text{As}_2\text{Sb})_2\text{S}_3$ layers where arsenic atoms are substituted homogeneously by antimony ones.

Density of samples in the investigated range of compositions has been measured. A non-linear increase of density with the antimony content was revealed. This result speaks in favor of clustering of a part of Sb_2S_3 structural units in glass. Microhardness of glassy samples has been determined. Microhardness raises slowly with the increase of Sb content as expected from the values of As-S and Sb-S bond energies. Nevertheless, a larger increase of As_2S_3 hardness was observed for the lowest concentration of Sb_2S_3 (5 at. %).

The powdered samples in the system were subjected to 30.5 hours irradiation by ultraviolet rays emitted by a medical UV lamp with the maximum emission on the wavelength 336 nm. As a consequence of UV radiation the As_2S_3 sample is partially transformed. Small amounts of crystalline As_2O_3 (arsenolite) has been detected by X-ray diffraction in pure As_2S_3 and in the sample doped with 5 at. % Sb_2S_3 . The samples with higher amount of Sb_2S_3 does not show any trace of As_2O_3 in the detection limit of X-ray diffractometer method. This observation speaks in favor of a greater stability against high energy radiation of the basic As_2S_3 glass doped by antimony. This feature is essential for applications in holography. The arsenic oxide drastically reduces the resolution of the registered images.

The study of the glassy pseudo-binary system $(\text{As}_2\text{S}_3)_{1-x}(\text{Sb}_2\text{S}_3)_x$ allows to conclude that its atomic scale structure is expressed by mixed As-S-Sb configurations and a small amount of Sb_2S_3 clusters. As a function of concentration, Sb_2S_3 stabilizes the structure of glassy As_2S_3 which becomes more resistant to UV radiation.

LASER PULSE EFFECTS IN Se-S GLASSY THICK FILMS

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Glassy thick films in the system Se-S can be easily prepared. The films exhibit high sensitivity to electromagnetic radiation in the range situated from infrared to ultraviolet part of the spectrum.

The photo-structural effects in the non-crystalline films of selenium sulphur alloys are accompanied by modifications of the optical parameters: optical transparency, diffusivity, change in the refractive index, etc. These modifications can be used as a physical basis for optical recording of information.

There were investigated the photo-induced effects in thick films of composition $\text{Se}_{1-x}\text{S}_x$ ($x = 0 - 0.8$) by irradiation with laser pulses of different intensities and wavelengths.

The characteristics of the photo-transformations induced in the investigated films depend essentially on the incident power density. For low power densities the photo-darkening phenomena predominate. For mean power densities crystallization processes do appear. For high power densities, clusters of bubbles are developed, due to evaporation phenomena occurring in the films. For very high, extreme values of the incident power densities the films are broken and a more or less localized degradation of the films is produced.

On the basis of the observed photo-induced modifications of the structure and properties of the non-crystalline films, specific to every composition selenium-sulphur, a process and system for optical recording of information was proposed.

ELECTRON-INDUCED CHANGES IN ABSORPTION EDGE FOR AMORPHOUS Ge-As-Se FILMS

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Thin films based on ternary chalcogenide glasses of Ge-As-Se family have attracted considerable interest because of the changes in their structure and electronic properties observed under thermal treatment and illumination. The structural changes should be expected also under the high-energy electron irradiation, resulting, e.g., from the displacement of atoms by the impact mechanism. Thin Ge-As-Se films are usually prepared in nonequilibrium conditions what is one of the reasons for the origination of chemical structure disordering. The experimental results on the effect of thermal treatment and high-energy electron (6.5 MeV) irradiation on the absorption edge for thin films obtained by thermal evaporation of bulk $(As_2Se_3)_{1-x}Ge_x$ ($x = 0.038 - 0.167$), $(As_2Se_3)_{1-y}(GeSe_2)_y$ ($y = 0.4 - 0.8$) glasses have been given. For these composition lines the character of the observed effects has been found to be different. The results of theoretical computations of the optical band gap for the investigated glass compositions carried out by the linear combination of atomic orbitals have been presented too. To account for the possible bond configurations in the investigated films the ordered bond network model and the random bond network model have been used. The mechanism for thermal and electron-induced changes in the structure and optical properties of the amorphous films under investigation has been discussed.

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FREQUENCY-RESOLVED PHOTOCONDUCTIVITY STUDIES IN AMORPHOUS AsSeSb AND AsSeTe

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Frequency-resolved photocurrent measurements (FRPC) were carried out on amorphous chalcogenide films such as AsSeSb and AsSeTe as a function of temperature (between 230 K and 395 K), and of excitation density of power (between 40 W/m^2 and 600 W/m^2), and in frequency range of 10Hz to $1.1 \times 10^4 \text{ Hz}$, yielding the lifetime distribution directly. The results indicate that the recombination is through *distant pairs*, since the lifetime does depend on the excitation density of power, through $\tau = AG^s$; as $\tau \propto G^{-0.46}$ at 295 K and $\tau \propto G^{-0.77}$ at 395 K, rather than by *geminate* (twin) pairs.

I_{ph} , the intensity of the photocurrent was found to depend on T (at fixed ω and G); on ω (at fixed T and G); and also on G (at fixed ω and T). The exponent s in the relationship $I_{ph} \propto \omega^s$ is found to depend on both temperature T and generation rate G in a manner such that the photocurrent will be more sensitive (inversely) to the frequency of excitation as either one of the above variables or both are lowered.

CORRELATION BETWEEN MECHANICAL PARAMETERS FOR AMORPHOUS CHALCOGENIDE FILMS

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Thin films deposited from chalcogenide vitreous semiconductors are used for IR optical coatings, data recording and other purposes in optoelectronics and microelectronics. Wear resistance dependent on mechanical properties and adhesion strength of the film - substrate combination is an important operational performance of thin film. In this work the data on the wear rate (ε), adhesion (σ_a) and shear (σ_{sh}) strength, initial mechanical stress (σ_0), microhardness (H_μ), flow limit (σ_f), Young's modulus (E) and linear thermal expansion coefficient for thermally deposited amorphous films of As_2S_3 , As_2Se_3 , $Ge_{28}Sb_{12}Se_{60}$, $Ge_{33}As_{12}Se_{55}$ and $Ge_{36}As_4S_{60}$ have been presented. The following correlation between the above-listed mechanical properties has been observed:

$$\varepsilon = 1.2 \times 10^{-6} \sigma_a, \quad \varepsilon = 1 + 1.2 \times 10^{-9} (EH_\mu)^{1/2}, \quad \sigma_{sh} = 1.2 \times 10^7 + 7.5 \times 10^{-3} (EH_\mu)^{1/2}, \quad \sigma_f = 0.06 H_\mu, \\ \sigma_a = 2 \times 10^6 + 0.15 \sigma_0.$$

Thermal spike in the zone of the contact (ΔT_c) resulting from the work done by frictional forces at the actual contact area and thickness of the thermal near-surface layer have been calculated. It has been shown, that in result of the originated significant compressive stress ($\sigma_{th} = E \alpha \Delta T_c$) exceeding the flow limit, the wear resistance of $Ge_{28}Sb_{12}Se_{60}$ films tends to diminish due to the decrease in their adhesion strength. The structural changes related to the drastic increase in temperature ΔT_c (because of the blistering effect) in the final stage of the wear testing have been found in these films. The direct proportionality between the wear rate and the calculated E_b/Ω_0 value (where E_b is the averaged bonding energy, Ω_0 - the averaged molar volume) has been found for the compositions under investigation. A correlation has been made between mechanical parameters (E , H_μ , α) of the bulk glasses and the relevant thin films and the possible reasons for the difference have been discussed.

ELECTRON – STIMULATED CHANGES IN OPTICAL – REFRACTOMETRIC PROPERTIES OF GLASSY SEMICONDUCTORS OF As-S(Se)-Ag(Hg)

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The detailed investigations of the influence of high-energy penetrating irradiation on chalcogenide glassy semiconductors (HGS) showed that the radiation stimulated changes in physical-chemical parameters and optical properties are also accompanied by substantial structural transformations. It is established that the radiation structural transformation mechanism is determined by the processes of formation of coordination defects, i.e. induced switching of chemical bonds: the accompanying relaxation processes can include the regions of the structure amounting to several interatomic distances (medium order).

In this paper the influence of the electron radiation with the energy of 30 KeV and 1.3 MeV on the optical, refractometric and acoustic-optical properties of monolithic samples of arsenic trisulphide and triselenide with Ag and Hg dopants was studied. The radiation-structural changes were studied by the methods of building the curves of induced optical density in the spectrum range of the fundamental absorption bands of the investigated HGS ($400-100\text{ cm}^{-1}$) and structural refractometry, and by the investigations of IR- absorption and Raman spectra.

It was found that the radiation-structural changes lead to a long-wave shift of the absorption edge by the value up to 0.05 eV and the refraction coefficient – up to 0.01. The observed changes in optical and refractometrical parameters are increasing during transition from selenide to sulphide; they depend to a great extent on Ag and Hg concentration and are determined by the intensity of an electron beam and radiation time. During repeated cycles of radiation annealing at the temperatures 20-20K lower than T_g the data of the change are of a reverse character. The irreversible component of the process conditioned by chemical interaction of matrix destruction products with the adsorbed dopants is increasing with the increase of the absorbed dose up to 2-8 MGr.

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ELECTRICAL RESISTIVITY MEASUREMENTS IN As-Te-In GLASSES UNDER PRESSURE: PRESSURE-INDUCED METALLIZATION AND EFFECT OF TOPOLOGICAL THRESHOLDS

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Bulk As-Te-In glasses have been prepared by melt-quenching method and DC electrical resistivity of these samples has been measured up to 8 GPa pressure in a Bridgman anvil set up. It is observed that electrical resistivity of $\text{As}_{40}\text{Te}_{60-x}\text{In}_x$ ($5 < x < 16.5$) glasses decreases continuously with pressure and reaches metallic values around 3.0 GPa. Electrical resistivity measurements as a function of temperature at different pressures also indicate that the activation energy of As-Te-In samples decreases with increase in pressure and the metallic state of the sample at high pressure is attained due to the decrease in energy gap under high pressure. It is interesting to note that the As-Te-In recovered from the cell remain amorphous even after subjecting to a pressure of 7 GPa. This shows that the observed resistivity transformation in As-Te-In glasses under pressure is from glassy semiconductor to glassy metal. The variation of normalised electrical resistivity at different pressures with composition suggests the possibility of Rigidity Percolation and Chemical Threshold occurring around an average coordination of $\langle r \rangle = 2.65$ and 2.70 respectively.

STRUCTURE, DIELECTRIC AND PHOTOELASTIC PROPERTIES OF Ge-Sb-S SYSTEM GLASSES

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Possibility of practical use of Ge-Sb-S system glasses in optical device building due to their high photosensitivity and transpanancy in near and middle region of IR spectrum evokes interest to their manysided study.

In the given work we present results of radial atoms distribution functions vibrational spectra, dielectric and photoelastic properties of Ge-Sb-S glasses system (cut of $(\text{Sb}_2\text{S}_3)_{1-x}(\text{GeS}_2)_x$).

We have calculated binar correlative functions and radial atoms distribution curves (RDF) using experimental curves intensity for X-ray scattering $I(s)$. On the curves $I(s)$ of the glasses in the compositions $0 < x < 0.3$ we state splitting of the main maximum (2.1 and 2.5 \AA^{-1}). In the same compositional region we notice anomalies on concentrational dependencies of density (ρ) and dielectric constant (ϵ). Under low s ($\sim 1.2 \text{ \AA}^{-1}$) function $I(s)$ shows maximum explained by big scattering structural complexes. RDF curves of $(\text{Sb}_2\text{S}_3)_{1-x}(\text{GeS}_2)_x$ glasses is characterized by three distinct maximums. Radius of the first coordinational sphere R_1 for Sb_2S_3 glass is 2.50 \AA . Increase of GeS_2 in glass composition leads to decrease of R_1 , which is 2.25 \AA for GeS_2 . Areas under RDF curves maximums and coordinational numbers are calculated.

It is stated that the main structural groups that form matrix of Sb_2S_3 - GeS_2 system glasses are pyramides $\text{SbS}_{3/2}$ and tetraeders $\text{GeS}_{4/2}$. In the structure of investigated glasses structural groups are defined in which homopolar Sb-Sb and S-S bonds are realized. Thegiven result is confirmed by the data of vibrational spectroscopy.

On the basis of photoelastic properties investigations Young's (E), shift (G) and bulk (K) modul were defined as well as Puasson index (μ) and adiabatic compressibility (α). It is stated that glasses with considerable content of GeS_2 are characterized by increased meaning of G and E. The cause of this is considerable level of connectedness in the glass structure on the basic of GeS_2 .

Anomalies on concentrational dependence ρ and ϵ in the compositional region $0 < x < 0.3$ are explained by a considerable deforming action of tetraedrical structural groups $\text{GeS}_{4/2}$ on glass matrix, built by trigonal pyramids $\text{SbS}_{3/2}$.

PECULIARITIES OF OBTAINING AND PROPERTIES OF GLASSY Sb CHALCOGENIDES

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The peculiar feature of glassy semiconductors is possibility to control their properties by changing their composition. But every time the frames of properties changes are limited by glassforming range in the system which borders have relative character. The process of glassformation is defined by melt cooling speed, which is limited by melt quantity and volume.

In the given work we submit the results of the investigation glassforming ranges, physical, chemical and thermodynamic parameters of glasses in Sb-S and Sb-Se systems.

Glassy alloys of the given system are obtained only in the conditions of intensive heat exchange and at melt cooling speed 50–300 K/s. Stable glasser terion in Sb-S system is within the limits from 35 to 50 at.% Sb, and in Sb-Se system it is to 25 at.%. X-ray phase and microstructural analyses showed the absence of crystalline inclusions in the obtained materials. Unstable conditions of metastable hardening defines formation of broad spectra of structural states that differ by types of chemical bonds between atoms, relative quantity homo- and heteropolar bonds, number of defects.

By the methods of thermal (TA) and difference-thermal (DTA) analyses we have defined glassformation temperature T_g , crystallization temperature T_c , melting temperature T_m of glasses and their dependence on heating speed. On the basis of the given investigations we have calculated activation energies of viscous flow E_η (60–80 kJ/mol – for glasses of Sb-S system, 50–75 kJ/mol – for Sb-Se) and activation energies for crystalline nucleus E_c (75–100 kJ/mol – for Sb-S, 60–105 kJ/mol – for Sb-Se). It is stated that the least crystalization possibility in Sb-S system belongs to eutectic alloys with little Sb quantity have the least crystalization possibility.

On the basis of TA and DTA data and results of investigation of physical and chemical parameters (ρ , H) of the glasses, metastable diagrams of Sb-S and Sb-Se system state were built.

Within temperature range 250–500 K and frequency range 10^4 – 10^8 Hz we have investigated temperature and frequency dependence of d.c. ($\sigma(0)$) and a.c. ($\sigma(\omega)$) conductivity and dielectric parameters (ϵ and $\text{tg}\delta$) of Sb-S and Sb-Se glasses systems. The mechanisms of charge transfer and polarization are proposed. We have determined influence of obtaining conditions on thermodynamic, physical, chemical and electrophysical glasses parameters.

VARIATION OF $\text{CdS}_{1-x}\text{Se}_x$ NANOCRYSTAL PARAMETERS UNDER HYDROSTATIC PRESSURE

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$\text{CdS}_{1-x}\text{Se}_x$ nanocrystals in glass matrices have become an object of extensive interest in view of wide possible applications as well as due to quantum-size effects arising from the spatial confinement of charge carriers. It is also interesting to investigate the variation of nanocrystal parameters under external factors, especially temperature and pressure.

The measurements of hydrostatic pressure effect upon the optical absorption spectra of $\text{CdS}_{1-x}\text{Se}_x$ ($x=0.6$, $r=2.76$ nm and $x=0.78$, $r=3.08$ nm) nanocrystals embedded in borosilicate glass matrix, are reported. The spectra were measured in a three-window optical pressure cell, benzene being used as a pressure medium. The pressure was varied in the range from 0 to 0.4 GPa in increasing and decreasing mode. At such pressures $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals of such size are known to possess wurtzite structure.

The increase of pressure is observed to result in a linear blue shift of the optical absorption edge of the nanocrystals by 4.09×10^{-2} eV/GPa for $\text{CdS}_{0.4}\text{Se}_{0.6}$ and 3.89×10^{-2} eV/GPa for $\text{CdS}_{0.22}\text{Se}_{0.78}$ samples. We could observe no noticeable shift or smearing of quantum-size related features in the spectra in the applied pressure range. The observed effects were the same in compression and decompression modes what indicates that $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals are in direct contact with the glass matrix. It should be noted that at normal conditions $\text{CdS}_{1-x}\text{Se}_x$ quantum dots in borosilicate glass already sustain hydrostatic pressure from the matrix caused by the specific features of their preparation. While being cooled from the synthesis temperature to room temperature the quantum dots are compressed by the matrix since the value of thermal expansion coefficient for the latter ($A=1.02 \cdot 10^{-5} \text{ K}^{-1}$) considerably exceeds those for II-VI semiconductors ($A_{\parallel}=2.6 \cdot 10^{-6} \text{ K}^{-1}$ and $A_{\perp}=4.6 \cdot 10^{-6} \text{ K}^{-1}$ for CdS; $A_{\parallel}=2.9 \cdot 10^{-6} \text{ K}^{-1}$ and $A_{\perp}=4.9 \cdot 10^{-6} \text{ K}^{-1}$ for CdSe). Taking into account the thermal expansion coefficients, from the optical absorption spectra of the samples under investigation, measured at 77 and 296 K, we have separated the pressure- and temperature-related contributions into the nanocrystal energy gap temperature variation.

The obtained parameters for nanocrystalline $\text{CdS}_{1-x}\text{Se}_x$ materials are important in view of their behaviour in annealing processes, which are applied for obtaining nanocrystals in glass matrices as well as for the studies of various external effects upon the nanocrystal properties.

FEATURES OF PHYSICOCHEMICAL INTERACTION IN THIN-FILM SYSTEM ON THE BASE OF ARSENIC TRISULPHIDE AND COPPER

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Thin-film systems based on chalcogenide glassy semiconductors (ChGS) and some metals (Ag, Cu) can be successfully applied in submicron lithography and are very promising in nanolithography as inorganic resists [1]. ChGS-Ag systems are among the most studied ones. The use of ChGS-Cu systems is difficult due to their chemical instability: the physico-chemical interactions between ChGS and copper are very intensive in them, which lead to formation of reaction product layer and their rapid aging. On the other hand, as recently was shown by us [2], the physico-chemical interaction in ChGS-metal systems can be applied for production of blazed holographic diffraction gratings. What is mentioned above requires detailed study of specific features of such interaction in thin-film ChGS-Cu systems.

The most universal physical property describing mass transport during interaction in such systems - amount of dissolved metal - was studied by the resistometrical method. Structural characteristics of Cu, As_2S_3 and $\text{As}_2\text{S}_3\text{-Cu}$ layers were studied by chemical dissolution, microscopy and ellipsometry.

Ellipsometric modeling results indicate that the thickness distribution of the dissolved copper is close to rectangular shape. It confirms reactionary nature of interaction. It was also shown that considerable variation of chemical process activity observed in thin-film $\text{As}_2\text{S}_3\text{-Cu}$ system is caused by essential dependence of physico-chemical interaction rate on ChGS film stoichiometry and imperfection of its structure. Application of thermochemical model for a probability estimation of quasi-molecular reactions of copper with polymerized and non-polymerized fragments of ChGS film enabled to give qualitative description of the interaction mechanism.

The results presented in this work indicate some new ways to control physico-chemical interaction process in ChGS-metal thin-film systems.

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FORMATION OF PROFILED HOLOGRAPHIC DIFFRACTION GRATINGS USING PHYSICOCHEMICAL INTERACTION IN As_2Se_3 -Ag SYSTEM

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Profiled holographic diffraction gratings (PHDG) combine the advantages of both the conventional holographic diffraction gratings (CHDG) with symmetrical grooves and the ruled ones: low scattering and high efficiency in a wavelength region around the designated wavelength. The simple method of PHDG fabrication by additional treatment of original gratings with symmetrical grooves have been developed.

The original holographic gratings were produced in As_2Se_3 layers deposited onto by thermal vacuum evaporation. Such chalcogenide media are characterized by high resolution capability, optical uniformity, sensitivity to the irradiation of available lasers, absence of shrinkage during post-exposure treatment. To produce a profiled grating, additional inclined vacuum deposition of thin Ag layer (1 - 10 nm) onto the relief pattern with symmetrical grooves is used. This technique is based on the physico-chemical interactions that take place when silver layer is vacuum-deposited onto chalcogenide glassy semiconductor (CGS) film. Such interaction begins during deposition and continues at a varied rate (depending on a specific Ag-CGS system) after the deposition process is terminated [1]. The rate of interaction between As_2Se_3 and Ag is one of the highest among CGS-Me systems. Metal penetrates into semiconductor to form a metal-enriched layer of reaction products. Etching rate of reaction products in alkaline solution is much lower than that for an undoped CGS film. Hence, in subsequent etching this layer served as a protective mask: unprotected regions of the As_2Se_3 film were etched off, and the grooves became asymmetrical.

The surface pattern of gratings was examined using a Dimension 3000 Scanning Probe Microscop (Digital Instruments). Computer modeling of transformation process of a symmetric grating into asymmetric one had been performed. To estimate the profiling effect, angular and spectral dependencies of diffraction efficiency for initial and transformed gratings were measured. The maximum value of absolute diffraction efficiency of the gratings reached 60% for non-polarized light in the spectral range corresponded to a blaze angle.

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PHOTOLUMINESCENCE STUDY OF CdS QUANTUM DOTS IN LANGMUIR-BLODGETT FILMS

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In this work the temperature dependence of stationary and time-resolved photoluminescence (PL) of CdS nanocrystals has been investigated. The nanocrystals were fabricated by the chemical interaction of Langmuir-Blodgett films of behenate cadmium with hydrogen sulfide and had their radii in the range of 1.5 to 6 nm with the mean radius of 3 nm and a density of $1 \cdot 10^{11} \text{ cm}^{-2}$.

Room-temperature stationary PL spectra of nanocrystals display a single wide band with its maximum at 420 nm. Low-temperature time-resolved measurements show that the band consists of two components which have different decay times. The boundary between the component bands coincides with the band-gap energy of bulk CdS. We attribute the «blue» component of the band to the recombination of excitons confined in CdS quantum dots, and the «red» component to the PL of the LB films. The transient PL decay reveals a non-exponential decay law across the whole temperature range 4.2–300 K studied. The decay curves can be fitted by a stretched-exponential function in the following form:

$$I_{PL}(t) = I_0 \exp(-(t/\tau)^\beta)$$

We found that the «blue» component of the PL band decays slower than the «red» one, its τ_b being equal to 1.3 μs at $T=5 \text{ K}$, while for the «red» band τ_r equals to 0.4 μs with approximately equal values of parameter $\beta \approx 0.35$. The excitonic decay time τ_b decreases with increasing temperature. The experimental data are interpreted in the model of spin-singlet and spin-triplet excitons which have different lifetimes and energy levels. The spin-singlet, spin-triplet lifetimes, and singlet-triplet splitting were estimated as functions of wavelength in this model.

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LIGHT INDUCED CHANGES IN THE OPTICAL PROPERTIES OF THIN As - S - Ge (Bi, Tl) FILMS

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Chalcogenide glasses are one of the most widely known families of amorphous materials and have been extensively studied for several decades, partly because of their interesting fundamental properties and partly because of their many potential applications in optical imaging, optical recording, infrared optics and, more recently, optical communications. In this paper we report results from studying changes in optical properties and microstructure of thin films from the systems $\text{As}_{1-x}\text{Ge}_x\text{S}_{60}$ ($0 \leq x \leq 40$) and $(\text{As}_2\text{S}_3)_{1-x}\text{Bi}(\text{Tl})_x$ ($0 \leq x \leq 15$) depending on the composition and conditions of evaporation and illumination to light. Conditions for synthesizing glasses with specific compositions have been established and thin layers, 100 and 1000 nm thick, simultaneously deposited onto glass, graphite and Si wafer substrates by thermal evaporation were investigated. The results of the X-ray microanalysis performed showed that the composition of bulk samples are very closed to the expected compositions, while difference was observed in the thin As - S - Tl layers due to the difficulties in thallium content determination. The optical transmission and reflection of thin layers (1000 nm thick) deposited on BK-7 optical glass substrates have been measured in the spectral region of 350 - 1500 nm and the refractive indices and optical band gap E_g^{opt} were calculated. It was found that the method of evaporation influences considerably the properties of thin chalcogenide films. The addition of Bi or Tl in As_2S_3 leads to an increase in the refractive index while Ge causes its decreasing. The illumination of as-deposited films causes an effect of photodarkening and decreasing in the optical band gap for As-containing films and photobleaching for As - Ge - S layers. Using TTR_m methods (R_m is the reflection of 100 nm thick films deposited on Si substrates), the thickness of thin layers from the systems As - S and As - S - Ge have been determined to an accuracy of ± 2 nm. At the same time, the accuracy in the determination of the refractive index, n , was less than ± 0.005 . For the absorption coefficient, k , around the absorption edge, it was about ± 0.01 , using a combination of TTR_m and TR methods. A comparison between the results obtained from the spectrophotometric and ellipsometric measurements has been made. The results confirm the viability of the methods used for determination the optical constants of very thin homogeneous films as well as for investigation of non-homogeneous thick chalcogenide coatings.

ANALYSIS OF a-SiO₂/ a-Si MULTILAYER STRUCTURES BY ION BEAM METHODS AND ELECTRON SPIN RESONANCE

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One model used to study the structure of silicon suboxide (SiO_x) layers is the random mixing model where a separation in Si-O₄ and Si-Si₄ phases is considered [1].

In order to analyze the applicability of the model, multilayered structures were deposited using a magnetron sputtering system, where Si atoms are sputtered in an Ar-O₂ mixture, by sequences of "put-on" and "put-off" the oxygen line during the deposition process. All samples have the same total thickness (250nm) and the thickness/layer is between 2 nm and 128 nm. The purpose of this paper is to investigate the inhomogeneity of these films and its limit.

The sample composition and thickness were investigated by conventional Rutherford backscattering spectrometry (RBS), high resolution RBS using a magnetic spectrograph and elastic recoil detection (ERD). The analysis of the conventional RBS and ERD spectra has revealed that samples with 16 layers and less are formed by a-Si/SiO₂ sequences. The high-resolution RBS measurements have also shown a multilayered structure for samples with 8 and respectively 4 nm /layer, but the composition of each layer is more SiO_x like, with different values of the x parameter. It seems that the interface region is dominant for samples with 4nm/layer and less. Possibly, the transition from a-Si region to a-SiO₂ layer is done via Si₃-Si-O and Si-Si-O₃ structural entities, which are more favorable from a chemical point of view [2].

The structural study is completed with the ESR measurements, which revealed two paramagnetic species. They showed very different saturation behaviors at high microwave powers. From the saturation properties and g - factors, the two species were attributed to a-Si dangling bonds and E' centers respectively. The latter are characteristic for SiO₂ material. We found that a-Si DBs are present in all samples, that is irrespective of the layers thickness. Their density amounts to about 10²⁰cm⁻³. In contrast, the concentration of the E' centers increases with the number of interfaces.

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AMORPHOUS TO CRYSTALLINE TRANSITIONAL EFFECTS ON ELECTRICAL BEHAVIOUR IN AMORPHOUS CHALCOGENIDE THIN FILMS

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Thin films of thicknesses $\approx 5000 \text{ \AA}$ have been deposited in a vacuum of $\approx 5 \times 10^{-6}$ Torr of the ternary $\text{Se}_{80}\text{Te}_{10}\text{Sb}_{10}$ bulk alloy pieces onto cleaned glass plates at room temperature by thermal evaporation technique. From the energy dispersive X-ray analysis (EDAX) patterns of the films, the presence of Se, Te and Sb in the desired proportion has been confirmed. A study of amorphous to crystalline transitional effect on the dark and photoconductivity measurements, the films are annealed above (state B) and below (state A) the crystallization temperature. X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements have been done in both states (A&B). Electron diffraction patterns reveal that the films are not amorphous but are polycrystalline (state B) in most of the regions. Transient photoconductivity measurements have been made at different temperatures, intensities and illumination times. The results indicate that dc conductivity (σ_{dc}) and photoconductivity (σ_{ph}) increase but the photosensitivity (σ_{ph}/σ_{dc}) decreases. A peak in the rise curve is observed and the decay is very fast (state A) whereas the photocurrent rises monotonically to the steady state value and the decay is quite slow (state B). For the detailed analysis of the photoconductive decay in state B, we have used the differential life time (τ_d) concept as suggested by Fuhs and Stuke (1) which shows that the recombination within localized states may be the predominant recombination mechanism in this state. The results are explained in terms of the defects in the mobility gap.

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EFFECT OF LIGHT INTENSITY AND TEMPERATURE ON THE TRANSIENT PHOTOCONDUCTIVITY IN THIN $a\text{-Se}_{80}\text{Te}_{20-x}\text{Cd}_x$

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The paper reports the transient photoconductivity measurements in thin amorphous $\text{Se}_{80}\text{Te}_{20-x}\text{Cd}_x$ ($x = 0, 0.5$, and 10 at%) films. Thin films of the glassy alloys have been prepared by vacuum evaporation technique at a base pressure $\approx 5 \times 10^{-6}$ Torr. Pre-deposited thick indium electrodes on well-degassed glass substrates have been used for electrical contacts. Rise and decay of photocurrent has been measured as a function of temperature, intensity and illumination times by shining monochromatic light of different wavelengths. It has been observed that the rise of photocurrent shows an anomalous behaviour in all concentrations of Cd impurities. After incorporating Cd into $\text{Se}_{80}\text{Te}_{20}$ binary alloy, the value of photoconductivity increases at 0.5 at % of Cd and decreases at 10 at% of Cd concentrations. It has been observed that the anomalous effect is larger in those conditions in which steady state photoconductivity (σ_{ph}) is also larger (as a result of increasing intensity or temperature). To assess the relative variation of the anomalous effect at various intensities and temperatures we define a quantity " $[E = \{\sigma_{ph(max)} - \sigma_{ph(st)}\} / \sigma_{ph(max)}]$ ". The value of E is larger at low concentration of Cd (0.5 at%) and smaller at higher concentration of Cd at all intensities and temperatures as compared to binary $\text{Se}_{80}\text{Te}_{20}$ alloy. Photosensitivity (σ_{ph}/σ_d) remains unchanged at low concentration but decreases quite significantly at higher concentration of Cd. The decay rate analysis shows that the decay rate is almost same at low concentration of Cd (0.5 at%) and increases at higher concentration of Cd (10 at%). At low concentration, impurity doping may take place while at higher concentration, the density of structural defects are increased. An increase in the anomalous behaviour at low concentration of Cd and decrease at higher concentration of Cd have been explained in terms of a recombination mechanism.

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THEORETICAL POSSIBILITY OF INCREASING OF SUPERCONDUCTIVITY TRANSITION TEMPERATURE IN HIGH TEMPERATURE SUPERCONDUCTORS BY REPLACING OXYGEN WITH CHALCOGENS

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In the present paper the experimental data which evidenced the increase of superconductivity transition temperature (T_c) in HTSC doped with chalcogens have been discussed. The interpretation of experimental data has been done in the frame of the negative-U centers model. It is supposed that if someone could replace large amount of oxygen with chalcogens (for example sulfur) the significant increasing of T_c can be obtained.

RESEMBLANCE OF LASER LIGHT AND ELECTRIC FIELD INFORMATION RECORDINGS ON CHALCOGENIDE GLASSY SEMICONDUCTORS

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"Crystal-glass" phase transition which is induced by laser light pulse (duration τ and power W) in thin films of chalcogenide semiconductors has been investigated in the paper [1-3]. The initial films consist of microcrystals and were more darker than glassy ones due to light scattering by microcrystals boundaries. Laser pulse focused in spot with square $\sim 10 \mu\text{m}^2$ has bleached locally film due to "crystal-glass" phase transition. The more power pulse has burned the film. It was discovered that for pulse with duration τ approximately less than $1 \mu\text{s}$ there was the wide pulse power interval $W_1(\tau) > W > W_2(\tau)$ when pulses induced "crystal-glass" phase transition without film destruction. Here the $W_1(\tau)$ and $W_2(\tau)$ are minimum powers needed for film destruction (burning) or bleaching by the factor two correspondingly. On τ increasing interval $W_1(\tau) - W_2(\tau)$ decreased and for $\tau > 10 \mu\text{s}$ became so narrow that bleaching without destruction was very difficult available. The similar results have been obtained when "crystal-glass" phase transition was induced by electric field pulses [4].

The present paper is devoted to discussion of above mentioned peculiarities of "crystal-glass" phase transition in thin films of chalcogenide glassy semiconductors from the point of view of information recording. It is emphasized that results of [1-4] show the strong resemblance between recordings with laser light and electric field and that the known advantages of optical and electrical recording and re-recording of information using shot pulses are possibly related to the existence of a wide power range $W_1(\tau) > W > W_2(\tau)$ for shot times.

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POSSIBLE HIGH TEMPERATURE SUPERCONDUCTIVITY IN CHALCOGENIDE GLASSY SEMICONDUCTORS

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The experimental evidences of possibly high temperature superconductivity in selenium, a glassy chalcogenide semiconductor, have been revealed and discussed for samples which consist of globules of well known HTSC $\text{YBa}_2\text{Cu}_3\text{O}_7$ composition which are embedded in glassy selenium matrix. The superconductivity possibly takes place in selenium channels with linear dimension of several microns which arise between $\text{YBa}_2\text{Cu}_3\text{O}_7$ globules due to switching effect. The parameters of channels determined for normal and superconducting state have been described by negative-U centers model rather well.

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MECHANISM OF PHOTOINDUCED CHANGES IN THE STRUCTURE AND OPTICAL PROPERTIES OF AMORPHOUS As_2S_3 FROM AB INITIO MOLECULAR ORBITAL CALCULATIONS

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We propose a mechanism of photostructural changes in amorphous As_2S_3 ($\alpha\text{-As}_2\text{S}_3$) on the basis of ab initio molecular orbital calculations on clusters of atoms modeling the local structure of the amorphous system. As a model of $\alpha\text{-As}_2\text{S}_3$, we employed a cluster of atoms containing seven AsS_3 trigonal pyramids; the H atoms in the cluster are used to saturate the dangling bonds of "surface" S atoms. The ground-state geometry of the cluster, which will be referred to as model 1, was obtained at the Hartree-Fock (HF) level using the 6-31G basis set augmented by a set of d functions. The calculated As-S bond distances (0.220 - 0.225 nm) and As-S-As bond angles (95 - 100 degrees) are in accordance with the observed values. The structural parameters obtained are in better agreement with those obtained for small clusters reported in a recent paper [Uchino, Clary and Elliott, Phys. Rev. Lett. **85**, 3305-3308 (2000)]. We also have found two other higher energy forms of the cluster, which can be regarded as metastable states. One is a cluster (model 2) having an electron-hole pair, in which a hole is localized at one of the As atom and an electron at its adjacent S atom. The interatomic distance between the hole-trapping As and electron-trapping S is 0.304 nm, which is substantially longer than the usual As-S bond distance. The other form of the cluster (model 3) consists of a five-fold coordinated As site having four As-S and one As-As bonds. We show that these two types of metastable structures (models 2 and 3) can be obtained as a result of a photoinduced structural transformation from the ground state (model 1). These photoinduced coordination defect centers in models 2 and 3 exhibit lower photoabsorption energies by 1-2 eV as compared with the usual pyramidal structure. Thus, we suggest that the present calculations give a theoretical basis for the observed photodarkening effect and photostructural changes in $\alpha\text{-As}_2\text{S}_3$.

NANO-SCALE ARRANGEMENT IN $\text{Ge}_x\text{As}(\text{Sb})_{40-x}\text{S}_{60}$ SYSTEMS

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The state of art of short- and medium range order arrangement in glasses and/or films of the $\text{Ge}_x\text{As}(\text{Sb})_{40-x}\text{S}_{60}$ systems is considered based on results obtained by IR, Raman, neutron and X-ray diffraction studies. The structural arrangement depends on the prevalence of the non-stoichiometric (Ge_2S_3) or stoichiometric (As_2S_3 or Sb_2S_3) components in the compositions and is defined in the frame of an extended pseudo-binary model. The main structural units form layer-like clusters or domains with different interconnections. With Ge-content increase a depolymerization and crosslinking by homopolar bonds lead to a transition from a two-to-three-dimensionality. The related increase of the disorder degree is confirmed by the Boson peak peculiarities. The 2D-3D transition is also visualized by peculiarities in the compositional dependences of optical band gap, refractive index, thermal diffusivity, microhardness, mechanical stress, solubility and heat capacity jump at a mean coordination number $Z \approx 2.67$ ($x \approx 27$). A minimum of the compactness near this transition corresponds to the largest "free volume", suitable for structural changes induced by heat, light, electron and γ -irradiation. These changes are larger in films of the Ge-As-S system characterized by essentially lower compactness, slightly higher repetitive distance (>0.5 nm) and correlation length (.2-3 nm), as defined by the FSDP parameters. The larger nano-scale rearrangement cause larger property changes. The maximal photobleaching and selective solubility, the nearly giant expansion by electron bombardment and the highest photoinduced anisotropy around the transition can be emphasized. Recent models of the induced scalar and vectoral effects are discussed, as well as the influence of the chemical ordering effect (near $x=0$).

The energy induced structural changes in the Ge-As-S system are suitable for applications. Positive photoresists with a maximal sensitivity for non-silver inorganic resists have been proposed. Antireflective coatings for light diodes with (or without) own photolithography have been proved in production conditions. Other perspective effects for optoelectronic purposes will be also proposed.

TIME-OF-FLIGHT TECHNIQUE FOR INVESTIGATION OF AMORPHOUS CHALCOGENIDES

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The traditional time-of-flight drift-mobility technique measures the time needed by carriers to transit through sample [1]. The modified time-of flight technique measure the charge-collection (G) and electrical field distribution $F_i(x)$ in space charge region of the structure metal - amorphous chalcogenides. The method of internal field profile measurement which uses the variation of the excitation wavelength and appled reverse field was described in [2]. The value of internal electric field is determined by external voltage $V_{G(V, \alpha)}$ under which $G(V, \alpha) = 0$ for a certain excitation wavelength (α is absorption efficiency, α is a function of wavelength and d is the sample thickness [2]).

$$F_i(x) = \frac{V_{G(V, \alpha)=0}}{d}, \quad (1)$$

We suggest the following equation for the definition of charge-collection

$$G(V, \alpha) = \frac{(1 - R(V, \alpha))\alpha\mu\tau}{(1 - \exp(-\alpha d))d} \times \int_0^d \frac{\exp(-\alpha x')}{x'' - x'} \left[\int_{x'}^{x''} (F_i(x) + \frac{V}{d}) dx \right] \left[1 - \exp \left(- \frac{d}{\frac{\mu\tau}{x'' - x'} \int_{x'}^{x''} (F_i(x) + \frac{V}{d}) dx} \right) \right] dx', \quad (2)$$

where μ is drift mobility of the carriers, τ is the lifetime, $R(V, \alpha)$ is the coefficient, which takes into consideration diffusion of the carriers against field, x'' is the co-ordinate of stop drift, and x' is the co-ordinate of carriers photogeneration. The co-ordinate x'' is defined by absorption efficiency and sample thickness, so that x'' is function of α and d .

The internal field profile and charge-collection are obtained directly from experiment. The data allow to calculate the value of $\mu\tau$ and distribution of the density localized states in mobility gap $N(E)$. So, this permits to obtain important parameters which characterize the material and the efficiency of the devices on its base.

The suggested modified time-of-flight technique allows to measure $\mu\tau$ for electrons and holes by changing the polarity of the applied voltage. Equation (2) unlike analogous one discussed in [3], takes in to account deep trapping by localized states during photogenerated charge drift. This gives the possibility to measure the internal field profile and to calculate the distribution of the density of localized states with more accuracy than the other classical methods.

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A NEW Ag-CONTAINING AMORPHOUS CHALCOGENIDE THIN FILMS - PROSPECTIVE MATERIALS FOR A REWRITABLE OPTICAL MEMORIES

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The technique of step-by-step optically-induced solid state reaction (OSSR) of Ag with $\text{As}_{33}\text{S}_{67}$ amorphous films has allowed to design films with exact silver concentration. The photodoped films with a silver concentration close to 25 at.%, i.e. with composition of the stoichiometric AgAsS_2 compound were prepared. The host $\text{As}_{33}\text{S}_{67}$ films were photodoped by consecutive dissolving thin (~ 10 nm) layer of silver, which resulted in a single-phase optically homogeneous films. We have analyzed affect of the silver doping in the host material on optical, thermal properties, and its structure by means of optical spectroscopy, temperature-modulated differential scanning calorimetry and Raman spectroscopy respectively.

The heat flow dependence on temperature was measured by DSC technique in heating scans and was applied to the AgAsS_2 amorphous film prepared by OSSR and to the AgAsS_2 melt-quenched glass. There is a clear evidence of the glass transition, crystallization and melting regions which are very similar for both samples. Small discrepancies can be explained by different particles size (crushed pieces of bulk glass and peeled thin film particles). Raman spectrum of AgAsS_2 films prepared by means of OSSR show the homogenous reaction products and the spectrum of the film represents almost identical structure of OSSR films as that of bulk glass of composition AgAsS_2 . It proves that photoinduced solid state reaction between silver and $\text{As}_{33}\text{S}_{67}$ could reach the same reaction products as it is during high temperature synthesis from elements in a melt.

The thermal behaviour of the film of composition AgAsS_2 clearly shows that OSSR can be used for the stable glass synthesis in a form of a homogeneous film. Application of such films can be foreseen for rewritable high resolution optical memories (reversible phase change "amorphous-crystalline" or film optical surface nanoshaping in dependence on intensity and silver concentration). The surface structure of optically shaped films were studied by atomic force microscopy.

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PHOTOLUMINESCENCE STUDY ON AMORPHOUS Ge-Se FILMS

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Light-induced structural changes are typical features of chalcogenide glasses, which have been widely applied to the information and energy fields. For example, the laser-induced effects in chalcogenide glasses have served as the base for rewritable optical data storage media, PD, CD-RW and DVD. And the gray- or multiple-scale responses in these materials permit an advent of novel rewritable optical memory, with higher density of storage and faster access speed. The knowledge of how light-excited electrons relax to the stable states will strongly promote the study on light-induced structural changes which have been discussed as photon-phonon cooperative processes.

Ge-Se glasses attract attention because of easy preparation and widely glass-forming range, where various structures can be obtained by different methods of preparation and subsequent treatments. Photoluminescence (PL) of melt-quenched $\text{Ge}_x\text{Se}_{1-x}$ glasses has a broad linewidth and a large Stokes shift, due to strong electron-lattice couplings. Here, we report the PL studies on vacuum-evaporated a- $\text{Ge}_x\text{Se}_{1-x}$ ($x=0.28-0.36$) films with the thickness of about 15 μm . We focus on the thermal annealing effects, a blue shift of the absorption coefficient, an increase of intensity of PL, and the changes of decay time and fatigue behavior. We also performed a Raman scattering measurement to determine the annealing effects on the local- and intermediate-range structures, particularly on the Ge-Ge and Se-Se homopolar bands. We eliminate the possibility of resonant Raman effect by varying excitation energy, and find that the thermal annealing is relevant to an increase of chemical order. The thermal annealing effect on a- GeSe_2 is considered as a reconstruction of the disordered amorphous structure of the a- GeSe_2 film, containing wrong bonds, Ge-Ge and Se-Se to a stable structure by diminishing the number of the wrong bonds and the related strain or internal pressure. According to the observations in the Ge-rich and Se-rich films, compared with the stoichiometric compound GeSe_2 , we conclude that the Se-Se contained local structures are probable the centers for the light-induced structural change events and the Ge-Ge structures, should cause a large randomness in as-deposited films which can be reduced by thermal annealing, provide channels for excited states relax to stable states without light emission. The relaxations of both the structure and the excited electrons are studied from the point of view of the relaxation and reconstruction of the short- and medium-range order.

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PREPARATION AND PROPERTIES OF GLASSES IN THE SYSTEM Se-I

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The system Se-I is important because there was found that halogens improve the electro-photographic process in the amorphous selenium films and, consequently, in xerox copying machines.

Bulk $\text{Se}_x\text{I}_{1-x}$ ($x = 0.1; 0.15; 0.20$) samples have been prepared by heating the corresponding amounts of high purity selenium and iodine in evacuated glass ampoules. Iodometric measurements have been used in monitoring the I/Se ratio after preparation and long storage of the samples at room temperature. Thermal analysis, X-ray diffraction, electrical conductivity and optical absorption measurements have been carried out.

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